(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 452 782 B1

(12) EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention of the grant of the patent:
15.01.1997 Bulletin 1997/03

(21) Application number: **91105637.2**

(22) Date of filing: **10.04.1991**

(51) Int. Cl.[6]: **C07D 207/404**, C07D 209/48, C07D 211/88, C07D 223/10, C07D 213/40, C07D 213/61, C07D 277/28, C07D 277/32, C07C 335/40

(54) Novel intermediates for preparing guanidine derivatives, their preparation and use

Neue Zwischenverbindungen zur Herstellung von Guanidinderivaten, ihre Herstellung und Verwendung

Nouveaux composés intermédiaires pour la préparation de dérivés de la guanidine, leur préparation et leur utilisation

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IT LI LU NL SE

(30) Priority: **13.04.1990 JP 98627/90**
17.08.1990 JP 217356/90

(43) Date of publication of application:
23.10.1991 Bulletin 1991/43

(73) Proprietor: **Takeda Chemical Industries, Ltd.**
Chuo-ku, Osaka (JP)

(72) Inventors:
- **Yasuyuki, Kando**
  Tsukuba, Ibaraki 305 (JP)
- **Hidekl, Uneme**
  Tsukuba, Ibaraki 305 (JP)
- **Isao, Minamida**
  Tsukuba, Ibaraki 305 (JP)

(74) Representative: **von Kreisler, Alek, Dipl.-Chem. et al**
Patentanwälte
von Kreisler-Selting-Werner
Postfach 10 22 41
50462 Köln (DE)

(56) References cited:
DD-A- 225 129
US-A- 4 287 346

- **CHEMICAL ABSTRACTS, vol. 89, no. 17, October 23, 1978 Columbus, Ohio, USA, CHUPP J.P. et al.: "Reactions of isocyanides with divalent sulfur containing heterocycles", page 603, columns 1,2, abstract no. 146820b.**

EP 0 452 782 B1

Printed by Rank Xerox (UK) Business Services
2.13.13/3.4

Description

FIELD OF THE INVENTION

The present invention relates to a process for preparing guanidine derivatives, intermediates for the preparation of the said guanidine derivatives, and a process for preparing the said intermediates. The said guanidine derivatives are useful as insecticides and miticides (see Japanese Patent Application No.333721/1989).

BACKGROUND OF THE INVENTION

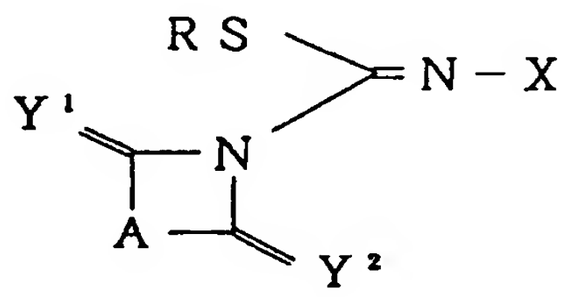
Heretofore, as a process for preparing N-substituted-N'-nitroisothiourea derivatives and N-cyclic(methyl)-N'-nitroisothiourea derivatives, which are useful as intermediates for the preparation of guanidine derivatives, there has been known a nitration process using sulfuric acid-fuming nitric acid for isothioureas [see "Journal of American Chemical Society," Vol. 76, p.1877, (1954)]. According to this known process, however, the yield in the nitration of isothioureas which have alkyl substituents on the nitrogen is extremely low and so this process has not been satisfactory as a general synthesis process or an industrial manufacturing process.

Further, U.S. Patent No. 4,287,346 discloses the preparation of cyanoguanidine derivatives by a substitution reaction of the corresponding isourea or isothiourea compound.

SUMMARY OF THE INVENTION

The present invention has been accomplished in view of the above-mentioned circumstances and it is the object thereof to find out novel synthetic intermediates for the preparation of N,N'-disubstituted isothiourea derivatives and N-cyclic (methyl)-N'-substituted isothiourea derivatives which are both useful as synthetic intermediates to guanidine derivatives, using a technique capable of being practiced industrially and economically in high yield, and to provide a process for preparing the said intermediates, as well as a process for preparing novel guanidine derivatives which are extremely useful as insecticides and miticides, using the said intermediates.

Having made extensive studies for attaining the above-mentioned subject, the present inventors found out that compounds represented by the following formula I



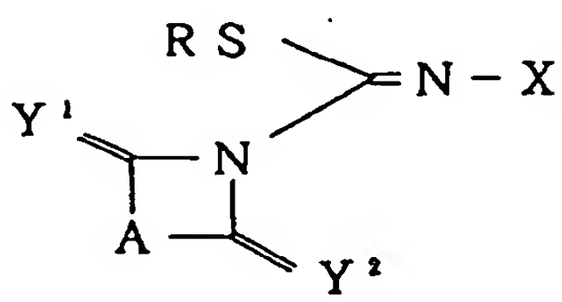
[I]

wherein R is a substituted or unsubstituted hydrocarbon radical or acyl group; X is an electron withdrawing group; Y^1 and Y^2, which are the same or different, are each independently oxygen or sulfur; and A is a substituted or unsubstituted divalent hydrocarbon residue, are highly reactive unexpectedly and that in these compounds the cyclic di(thio)acylimide moiety is preferentially substituted by amines, followed by a substitution reaction of the RS moiety:

As a result of these studies, we have now completed the present invention.

The present invention relates to

(1) a compound of the formula [I]



[I]

wherein

R is C_{1-10} alkyl (straight, branched or cyclic), C_{2-10} alkenyl, C_{2-10} alkynyl, C_{7-12} aralkyl, or C_{1-10} acyl (aliphatic, alicyclic, aromatic, or heterocyclic), which may be optionally substituted with one to five same or different substituents selected from

C_{3-10} cycloalkyl, C_{3-10} cycloalkenyl, C_{6-10} aryloxy, C_{6-10} arylthio, C_{6-10} arylsulfinyl, C_{6-10} arylsulfonyl, C_{6-10} arylamino, thienyl, furyl, pyrazolyl, thiazolyl, isothiazolyl, oxazolyl, isoxazolyl, imidazolyl, triazolyl, tetrazolyl, pyridyl, pyrimidinyl, pyridazinyl, quinolyl, isoquinolyl, indolyl, and (in case of R being C_{7-12} aralkyl and C_{1-10} acyl) C_{6-10} aryl and C_{7-10} aralkyl,

C_{2-10} alkenyl, C_{2-10} alkynyl, C_{1-4} alkoxy, C_{1-4} alkylthio, C_{1-4} alkylsulfinyl, C_{1-4} alkylsulfonyl, amino, mono- or di-C_{1-4} alkylamino, C_{3-6} cycloalkylamino, and (in case of R being C_{7-12} aralkyl and C_{1-10} acyl) C_{1-15} alkyl,

nitro, hydroxyl, mercapto, oxo, thioxo, cyano, carbamoyl, carboxyl, C_{1-4} alkoxycarbonyl, sulfo, halogen, C_{2-6} acylamino, C_{2-4} acyl, and C_{6-10} arylcarbonyl;

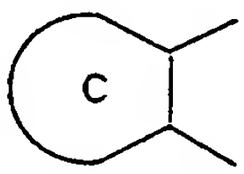
X is an electron withdrawing group selected from cyano, nitro, alkoxycarbonyl, hydroxycarbonyl, C_{6-10} aryloxycarbonyl, C_{1-4} alkylsulfonyl (optionally substituted with halogen), sulfamoyl, diC_{1-4} alkoxyphosphoryl, C_{1-4} acyl (optionally substituted with halogen), carbamoyl, C_{1-4} alkylsulfonylthiocarbamoyl, thienyloxycarbonyl, furyloxycarbonyl, pyrazolyloxycarbonyl, thiazolyloxycarbonyl, isothiazolyloxycarbonyl, oxazolyloxycarbonyl, isoxazolyloxycarbonyl, imidazolyloxycarbonyl, triazolyloxycarbonyl, tetrazolyloxycarbonyl, pyridyloxycarbonyl, pyrimidinyloxycarbonyl, pyridazinyloxycarbonyl, quinolyloxycarbonyl, isoquinolyloxycarbonyl, and indolyloxycarbonyl;

Y^1 and Y^2, which are the same or different, are each independently oxygen or sulfur; and

A is a divalent hydrocarbon residue selected from C_{1-4} alkylene,

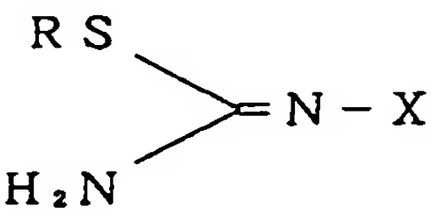
and a cyclic group

represented by the following formula:



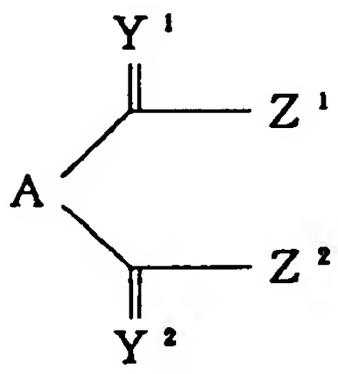
wherein the C-ring represents benzene or cyclohexane;

(2) a process for preparing a compound of the formula [I], which comprises reacting a compound of the formula



[II]

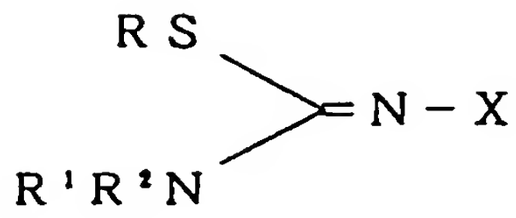
wherein R and X are as defined previously, with a compound of the formula



[III]

wherein A, Y^1 and Y^2 are as defined previously, Z^1 and Z^2, which are the same or different, are selected from fluorine, chlorine, and bromine halogen or Z^1 and Z^2 taken together represent oxygen;

(3) a process for preparing a compound of the following formula or a salt thereof:



[V]

wherein R and X are as defined previously, R^1 and R^2, which are the same or different, are each independently hydrogen, C_{1-10} alkyl (straight, branched, or cyclic), C_{2-10} alkenyl, C_{2-10} alkynyl, or C_{7-12} aralkyl, which may be optionally substituted with one to five same or different substituents selected from

C_{3-10} cycloalkyl, C_{3-10} cycloalkenyl, C_{6-10} aryloxy, C_{6-10} arylthio, C_{6-10} arylsulfinyl, C_{6-10} arylsulfonyl, C_{6-10} arylamino, thienyl, furyl, pyrazolyl, thiazolyl, isothiazolyl, oxazolyl, isoxazolyl, imidazolyl, triazolyl, tetrazolyl, pyridyl, pyrimidinyl, pyridazinyl, quinolyl, isoquinolyl, indolyl, and (in case of R^1 and R^2 being C_{7-12} aralkyl) C_{6-10} aryl and C_{7-10} aralkyl, [said group of substituents being optionally substituted with 1 to 5 same or different substituents selected from halogen, hydroxyl, C_{1-4} alkyl, C_{2-4} alkenyl, C_{2-4} alkynyl, C_{6-10} aryl, C_{1-4} alkoxy, phenoxy, C_{1-4} alkylthio, and phenylthio],

C_{2-10} alkenyl, C_{2-10} alkynyl, C_{1-4} alkoxy, C_{1-4} alkylthio, C_{1-4} alkylsulfinyl, C_{1-4} alkylsulfonyl, amino, mono- or di-C_{1-4} alkylamino, C_{3-6} cycloalkylamino, and (in case of R^1 and R^2 being C_{7-12} aralkyl) C_{1-15} alkyl, [said group of substituents being optionally substituted with 1 to 5 same or different substituents selected from

halogen, hydroxyl, C_{1-4} alkoxy and C_{1-4} alkylthio],

nitro, hydroxyl, mercapto, oxo, thioxo, cyano, carbamoyl, carboxyl, C_{1-4} alkoxycarbonyl, sulfo, halogen, C_{2-6} acylamino, C_{2-4} acyl, and C_{6-10} arylcarbonyl; or

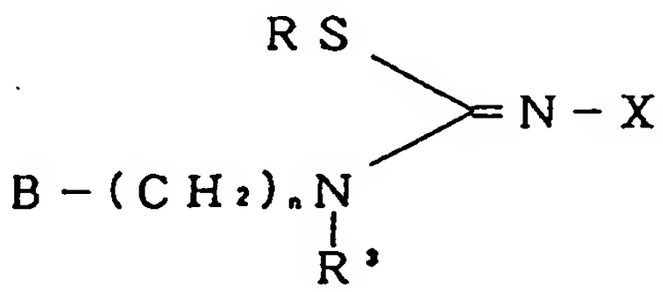
R^1 and R^2 taken together with the vicinal nitrogen represent an aziridino, azetidino, pyrrolidino, morpholino, or thiomorpholino group,

which comprises reacting a compound of the formula [I] with an amine of the following formula or a salt thereof:

$$R^1R^2NH \qquad [VI]$$

wherein R^1 and R^2 are as defined above;

(4) a process for preparing a compound of the following formula or a salt thereof:



[VII]

wherein R and X are as defined above;

n is 0 or 1;

B is C_{3-8} cycloalkyl, C_{3-8} cycloalkenyl, or C_{6-14} aryl, thienyl, furyl, pyrrolyl, pyridyl, oxazolyl, thiazolyl, pyrazolyl, imidazolyl, isoxazolyl, isothiazolyl, oxadiazolyl, thiadiazolyl, triazolyl, tetrazolyl, N-oxide-pyridyl, pyrimidinyl, N-oxide-pyrimidinyl, pyridazinyl, pyrazinyl, N-oxide-pyrazinyl, N-oxide-pyridazinyl, benzofuryl, benzothienyl, benzothiazolyl, benzoxazolyl, triazinyl, oxo-triazinyl, tetrazolo[1,5-b]pyridazinyl, triazolo[4,5-b]pyridazinyl, oxo-imidazolyl, dioxo-triazinyl, pyrrolidinyl, piperidyl, pyranyl, thiopyranyl, oxazinyl, morpholinyl, thiazinyl, piperazinyl, benzoimidazolyl, quinolyl, isoquinolyl, cinnolinyl, phthalazinyl, quinazolinyl, quinoxalinyl, indolizinyl, quinolizinyl, 1,8-naphthyridinyl, purinyl, pteridinyl, dibenzofuranyl, carbazolyl, acridinyl, phenanthridinyl, phenazinyl, phenothiazinyl, and phenoxazinyl, which may be optionally substituted with one to five same or different substituents selected from

C_{1-15} alkyl, C_{6-10} aryl, C_{7-10} aralkyl, C_{3-10} cycloalkyl, C_{2-10} alkenyl, C_{2-10} alkynyl, C_{3-10} cycloalkenyl, nitro, hydroxyl, mercapto, oxo, thioxo, cyano, carbamoyl, carboxyl, C_{1-4} alkoxycarbonyl, sulfo, halogen, C_{1-4} alkoxy, C_{6-10} aryloxy, C_{1-4} alkylthio, C_{6-10} arylthio, C_{1-4} alkylsulfinyl, C_{6-10} arylsulfinyl, C_{1-4} alkylsulfonyl, C_{6-10} arylsulfonyl, amino, C_{2-6} acylamino, mono- or di-C_{1-4} alkylamino, C_{3-6} cycloalkylamino, C_{6-10} arylamino, C_{2-4} acyl, C_{6-10} arylcarbonyl, thienyl, furyl, pyrazolyl, thiazolyl, isothiazolyl, oxazolyl, isoxazolyl, imidazolyl, triazolyl, tetrazolyl, pyridyl, pyrimidinyl, pyridazinyl, quinolyl, isoquinolyl, and indolyl; and

R^3 is hydrogen, C_{1-10} alkyl (straight, branched or cyclic), C_{2-10} alkenyl, C_{2-10} alkynyl, or C_{7-12} aralkyl, which may be optionally substituted with one to five same or different substituents selected from

C_{3-10} cycloalkyl, C_{3-10} cycloalkenyl, C_{6-10} aryloxy, C_{6-10} arylthio, C_{6-10} arylsulfinyl, C_{6-10} arylsulfonyl, C_{6-10} arylamino, thienyl, furyl, pyrazolyl, thiazolyl, isothiazolyl, oxazolyl, isoxazolyl, imidazolyl, triazolyl, tetrazolyl, pyridyl, pyrimidinyl, pyridazinyl, quinolyl, isoquinolyl, indolyl, and (in case of R^3 being C_{7-12} aralkyl) C_{6-10} aryl and C_{7-10} aralkyl, [said group of substituents being optionally substituted with 1 to 5 same or different substituents selected from halogen, hydroxyl, C_{1-4} alkyl, C_{2-4} alkenyl, C_{2-4} alkynyl, C_{6-10} aryl, C_{1-4} alkoxy, phenoxy, C_{1-4} alkylthio, and phenylthio],

C_{2-10} alkenyl, C_{2-10} alkynyl, C_{1-4} alkoxy, C_{1-4} alkylthio, C_{1-4} alkylsulfinyl, C_{1-4} alkylsulfonyl, amino, mono- or di-C_{1-4} alkylamino, C_{3-6} cycloalkylamino, and (in case of R^3 being C_{7-12} aralkyl) C_{1-15} alkyl, [said group of substituents being optionally substituted with 1 to 5 same or different substituents selected from

halogen, hydroxyl, C_{1-4} alkoxy and C_{1-4} alkylthio],

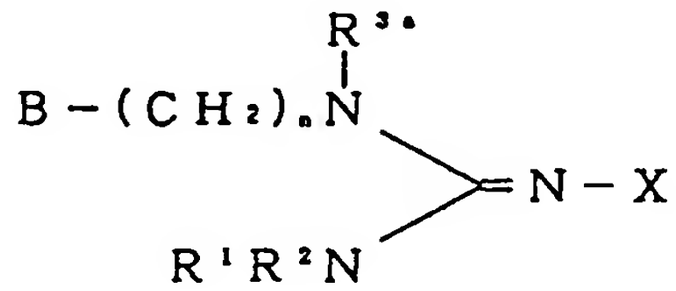
nitro, hydroxyl, mercapto, oxo, thioxo, cyano, carbamoyl, carboxyl, C_{1-4} alkoxycarbonyl, sulfo, halogen, C_{2-6} acylamino, C_{2-4} acyl, and C_{6-10} arylcarbonyl, which

comprises reacting a compound of the formula [I] with a compound of the following formula or a salt thereof:

$$R^3\text{-}NH(CH_2)_n\text{-}B \qquad [VI]$$

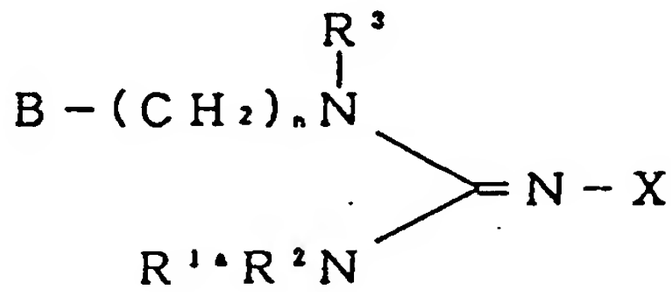
wherein R^3, n and B are as defined above;

(5) a process for preparing a compound of the following formula or a salt thereof:



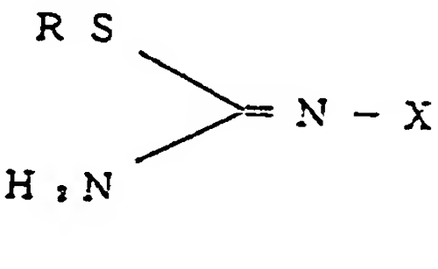
[IX]

or

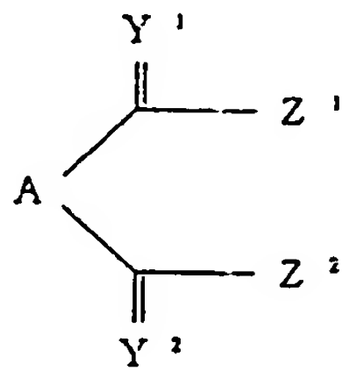


[VIII]

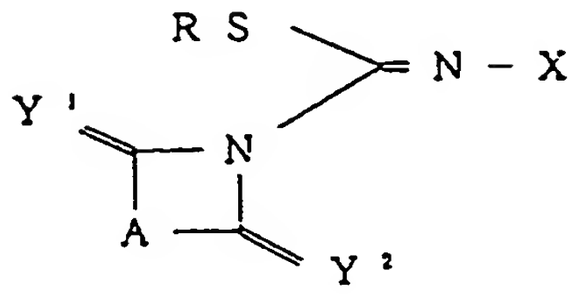
which comprises reacting a compound of the following formula:



with a compound of the following formula:



and then reacting the compound produced having the following formula



i) with an amine having the formula:

$$R^1R^2NH$$

or a salt thereof followed by reaction of a compound of the formula:

$$R^3\text{-}NH(CH_2)_n\text{-}B$$

after acylation if necessary when R^1 represents a hydrogen atom; or
ii) with a compound of the formula:

$$R^3\text{-}NH(CH_2)_n\text{-}B$$

followed by reaction of an amine having the formula

$$R^1R^2NH$$

or a salt thereof, after acylation if necessary when R^3 represents a hydrogen atom,
wherein A, R, X Y^1,
Y^2, B, n, R^1, R^2,R^3, Z^1 and Z^2 are as defined above;

R^{1a} is of the same meaning as R^1, and additionally can be $C_{1\text{-}10}$ acyl (aliphatic, alicyclic, aromatic, or heterocyclic), which may be optionally substituted with one to five same or different substituents selected from

$C_{3\text{-}10}$ cycloalkyl, $C_{3\text{-}10}$ cycloalkenyl, $C_{6\text{-}10}$ aryloxy, $C_{6\text{-}10}$ arylthio, $C_{6\text{-}10}$ arylsulfinyl, $C_{6\text{-}10}$ arylsulfonyl, $C_{6\text{-}10}$ arylamino, $C_{6\text{-}10}$ aryl, $C_{7\text{-}10}$ aralkyl, thienyl, furyl, pyrazolyl, thiazolyl, isothiazolyl, oxazolyl, isoxazolyl, imidazolyl, triazolyl, tetrazolyl, pyridyl, pyrimidinyl, pyridazinyl, quinolyl, isoquinolyl, and indolyl, [said group of substituents being optionally substituted with 1 to 5 same or different substituents selected from halogen, hydroxyl, $C_{1\text{-}4}$ alkyl, $C_{2\text{-}4}$ alkenyl, $C_{2\text{-}4}$ alkynyl, $C_{6\text{-}10}$ aryl, $C_{1\text{-}4}$ alkoxy, phenoxy, $C_{1\text{-}4}$ alkylthio, and phenyltio],

$C_{2\text{-}10}$ alkenyl, $C_{2\text{-}10}$ alkynyl, $C_{1\text{-}4}$ alkoxy, $C_{1\text{-}4}$ alkylthio, $C_{1\text{-}4}$ alkylsulfinyl, $C_{1\text{-}4}$ alkylsulfonyl, amino, mono- or di-$C_{1\text{-}4}$ alkylamino, $C_{3\text{-}6}$ cycloalkylamino, $C_{1\text{-}15}$ alkyl, [said group of substituents being optionally substituted with 1 to 5 same or different substituents selected from

halogen, hydroxyl, $C_{1\text{-}4}$ alkoxy and $C_{1\text{-}4}$ alkylthio],

nitro, hydroxyl, mercapto, oxo, thioxo, cyano, carbamoyl, carboxyl, $C_{1\text{-}4}$ alkoxycarbonyl, sulfo, halogen, $C_{2\text{-}6}$ acylamino, $C_{2\text{-}4}$ acyl, and $C_{6\text{-}10}$ arylcarbonyl; or
R^{1a} and R^2 taken together with the vicinal nitrogen represent a cyclic amino group; and
R^{3a} is of the same meaning as R^3, and additionally can be $C_{1\text{-}10}$ acyl (aliphatic, alicyclic, aromatic, or heterocyclic), which may be optionally substituted with one to five same or different substituent groups selected from

$C_{3\text{-}10}$ cycloalkyl, $C_{3\text{-}10}$ cycloalkenyl, $C_{6\text{-}10}$ aryloxy, $C_{6\text{-}10}$ arylthio, $C_{6\text{-}10}$ arylsulfinyl, $C_{6\text{-}10}$ arylsulfonyl, $C_{6\text{-}10}$ arylamino, $C_{6\text{-}10}$ aryl, $C_{7\text{-}10}$ aralkyl, thienyl, furyl, pyrazolyl, thiazolyl, isothiazolyl, oxazolyl, isoxazolyl, imidazolyl, triazolyl, tetrazolyl, pyridyl, pyrimidinyl, pyridazinyl, quinolyl, isoquinolyl, and indolyl, [said group of substituents being optionally substituted with 1 to 5 same or different substituents selected from halogen, hydroxyl, $C_{1\text{-}4}$ alkyl, $C_{2\text{-}4}$ alkenyl, $C_{2\text{-}4}$ alkynyl, $C_{6\text{-}10}$ aryl, $C_{1\text{-}4}$ alkoxy, phenoxy, $C_{1\text{-}4}$ alkylthio, and phenylthio],

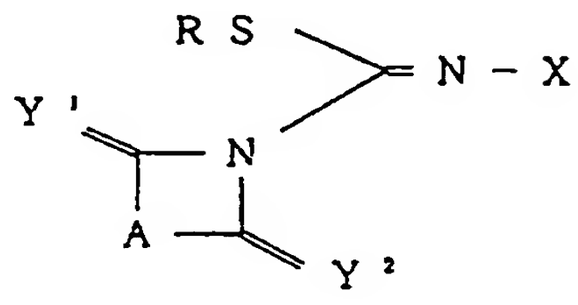
$C_{2\text{-}10}$ alkenyl, $C_{2\text{-}10}$ alkynyl, $C_{1\text{-}4}$ alkoxy, $C_{1\text{-}4}$ alkylthio, $C_{1\text{-}4}$ alkylsulfinyl, $C_{1\text{-}4}$ alkylsulfonyl, amino, mono- or di-$C_{1\text{-}4}$ alkylamino, $C_{3\text{-}6}$ cycloalkylamino, $C_{1\text{-}15}$ alkyl, [said group of substituents being optionally substituted with 1 to 5 same or different substituents selected from

halogen, hydroxyl, $C_{1\text{-}4}$ alkoxy and $C_{1\text{-}4}$ alkylthio],

nitro, hydroxyl, mercapto, oxo, thioxo, cyano, carbamoyl, carboxyl, $C_{1\text{-}4}$ alkoxycarbonyl, sulfo, halogen, $C_{2\text{-}6}$

acylamino, C_{2-4} acyl, and C_{6-10} arylcarbonyl;

(6) a process for preparing the compounds of formula [VIII] or [IX] which comprises reacting a compound of the following formula:



i) with an amine having the formula:

$$R^1R^2NH$$

or a salt thereof followed by reaction of a compound of the formula:

$$R^3\text{-}NH(CH_2)_n\text{-}B$$

after acylation if necessary when R^1 represents a hydrogen atom; or

ii) with a compound of the formula:

$$R^3\text{-}NH(CH_2)_n\text{-}B$$

followed by reaction of an amine having the formula

$$R^1R^2NH$$

or a salt thereof, after acylation if necessary when R^3 represents a hydrogen atom,

where all the symbols are as defined above.

The intermediate compounds [I] according to the present invention are excellently reactive and advantageously selective, thereby being useful in the preparation of valuable guanidine insecticides and miticides.

DETAILED DESCRIPTION OF THE INVENTION

According to the present invention, there are provided novel compounds of the formula [I] and novel processes for preparing compounds of the formulas [V], [VII], [VIII], and [IX] by use of the compound [I].

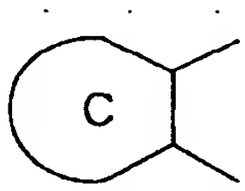
Further, the present invention provides processes for producing the compound [I] which is of value in the preparation of insecticidal and miticidal guanidine derivatives.

As substituent R in the above formulae there are mentioned C_{1-10} alkyl groups, C_{2-10} alkenyl groups, C_{2-10} alkynyl groups, C_{7-12} aralkyl groups, and C_{1-10} acyl groups, all of which may be substituted. Said C_{1-10} acyl group may be aliphatic, alicyclic, aromatic, or heterocyclic as mentioned herein below. Examples of C_{1-10} alkyl groups in the substituent R include straight-chain alkyl groups such as methyl, ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, and n-decyl; branched alkyl groups such as i-propyl, i-butyl, s-butyl, t-butyl, i-pentyl, s-pentyl, t-pentyl, i-hexyl, s-hexyl, and t-hexyl; and cyclic alkyl groups such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, and cycloheptyl. Examples of C_{2-10} alkenyl groups for R include vinyl, allyl, 2-butenyl, and 1-pentenyl. Examples of C_{2-10} alkynyl groups for R include 1-ethynyl, propargyl, 2-butynyl, and 1-pentynyl. Examples of C_{1-10} acyl groups for R include straight-chain C_{1-10} acyl groups such as formyl, acetyl, and propionyl, as well as acyl groups obtained by substituting the valence-side end methylene group in each of the alkyl groups exemplified above as C_{1-10} alkyl groups with carbonyl group. Examples of C_{7-12} aralkyl groups for R include benzyl, 1-phenethyl, 2-phenethyl, 1-naphthylmethyl, and 2-naphthylmethyl. These C_{1-10} alkyl, C_{2-10} alkenyl, C_{2-10} alkynyl, C_{1-10} acyl and C_{7-12} aralkyl groups for R may each contain one to five same or different substituent groups. As such substituent groups there are mentioned C_{3-10} cycloalkyl groups such as cyclopropyl, cyclobutyl, cyclopentyl, and cyclohexyl; C_{2-10} alkenyl groups such as vinyl, allyl, 2-methylallyl, 2-butenyl, 3-butenyl, and

3-octenyl; C_{2-10} alkynyl groups such as ethynyl, 2-propynyl, and 3-hexynyl; C_{3-10} cycloalkenyl groups such as cyclopropenyl, cyclopentenyl, and cyclohexenyl; nitro, hydroxyl, mercapto, oxo, thioxo, cyano, carbamoyl, carboxyl; C_{1-4} alkoxycarbonyls such as methoxycarbonyl and ethoxycarbonyl; sulfo; halogens such as fluorine, chlorine, bromine and iodine; C_{1-4} alkoxy groups such as methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, s-butoxy, and t-butoxy; C_{6-10} aryloxy groups such as phenoxy; C_{1-4} alkylthio groups such as methylthio, ethylthio, n-propylthio, isopropylthio, n-butylthio, and t-butylthio; C_{6-10} arylthio groups such as phenylthio; C_{1-4} alkylsulfinyl groups such as methylsulfinyl and ethylsulfinyl; C_{6-10} arylsulfinyl groups such as phenylsulfinyl; C_{1-4} alkylsulfonyl groups such as methylsulfonyl and ethylsulfonyl; C_{6-10} arylsulfonyl groups such as phenylsulfonyl; amino; C_{2-6} acylamino groups such as acetylamino and propionylamino; mono- or di-C_{1-4} alkylamino groups such as methylamino, ethylamino, n-propylamino, isopropylamino, n-butylamino, dimethylamino, and diethylamino; C_{3-6} cycloalkylamino groups such as cyclohexylamino; C_{6-10} arylamino groups such as anilino; C_{2-4} acyl such as acetyl; C_{6-10} arylcarbonyl such as benzoyl; as well as five- to six-membered heterocyclic groups selected from 2- or 3-thienyl, 2- or 3-furyl, 3-, 4- or 5-pyrazolyl, 2-, 4- or 5-thiazolyl, 3-, 4- or 5-isothiazolyl, 2-, 4- or 5-oxazolyl, 3-, 4- or 5-isoxazolyl, 2-, 4- or 5-imidazolyl, 1,2,3- or 1,2,4-triazolyl, 1H- or 2H-tetrazolyl, 2-, 3- or 4-pyridyl, 2-, 4- or 5-pyrimidinyl, 3- or 4-pyridazinyl, quinolyl, isoquinolyl, and indolyl. In the case where R is a substituted C_{7-12} aralkyl or a substituted C_{1-10} acyl, there are mentioned, as examples of the substituent group, C_{1-15} alkyl groups such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, s-butyl, t-butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, and pentadecyl; C_{6-10} aryl groups such as phenyl and naphthyl; and C_{7-10} aralkyl groups such as benzyl and phenylethyl.

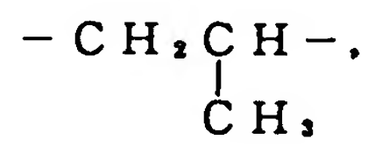
Preferred examples of R are C_{1-4} alkyl groups such as methyl and ethyl and C_{7-10} aralkyl groups such as benzyl.

As divalent hydrocarbon residue A in the foregoing formulae there are mentioned C_{1-4} alkylene and a cyclic group represented by the following formula:

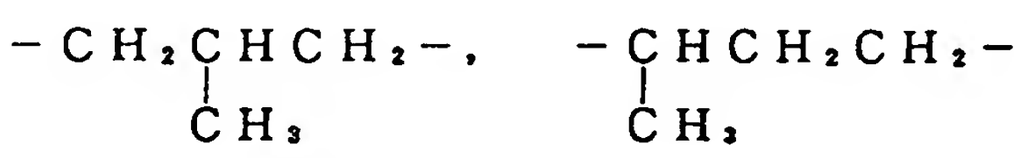


wherein the C-ring represents benzene or cyclohexane.

As examples of the C_{1-4} alkylene groups there are mentioned - CH_2-, -CH_2CH_2-, -$CH_2CH_2CH_2$-,



-$(CH_2)_4$-,



Preferred examples of A in the foregoing formulae are o-phenylene, 1,2-ethylene and 1,3-propylene.

In the foregoing formula, Y^1 and Y^2 are the same or different and each represent independently oxygen or sulfur atom, with oxygen being preferred.

The electron withdrawing group as X in the foregoing formulae include cyano, nitro, alkoxycarbonyl (e.g. C_{1-4} alkoxycarbonyl such as methoxycarbonyl and ethoxycarbonyl), hydroxycarbonyl, C_{6-10} aryloxycarbonyl (e.g. phenoxycarbonyl), heterocycloxycarbonyl (as the heterocyclic group there may be used any of those exemplified above; e.g. pyridyloxycarbonyl, thienyloxycarbonyl), C_{1-4} alkylsulfonyl (e.g. methylsulfonyl, trifluoromethylsulfonyl, ethylsulfonyl) which may be substituted with halogen (e.g. Cl, Br) for example, sulfamoyl, di-C_{1-4} alkoxyphosphoryl (e.g. diethoxyphosphoryl), C_{1-4} acyl (e.g. acetyl, trichloroacetyl, trifluoroacetyl) which may be substituted with halogen (e.g. Cl, Br) for example, carbamoyl, and C_{1-4} alkylsulfonylthiocarbamoyl (e.g. methylsulfonylthiocarbamoyl). Nitro is one of preferred electron withdrawing groups.

Z^1 and Z^2 in the foregoing formulae are the same or different and represent each a halogen atom selected from fluorine chlorine, or bromine atom, or taken together represent an oxygen atom. Halogens, e.g. chlorine atom, are preferred examples of Z^1 and Z^2.

In the foregoing formulae, regarding the substituted or unsubstituted hydrocarbon radicals in the definitions of R^1,

R^2, R^3, R^{1a} and R^{3a}, as examples of the hydrocarbon radicals there are mentioned those referred to above in connection with the substituent R (particularly C_{1-10} alkyl, C_{2-10} alkenyl and C_{2-10} alkynyl, which may be straight-chain, branched, or cyclic). As examples of the substituent group in the said "substituted or unsubstituted hydrocarbon residues" there are mentioned those exemplified above in connection with the substituent R. In the case where R^1 and R^2 taken together with the vicinal nitrogen represent a cyclic amino group, there are mentioned aziridino, azetidino, pyrrolidino, morpholino, and thiomorpholino. As examples of the acyl group in the definitions of R^{1a} and R^{3a} there are mentioned those exemplified above in connection with the substituent R.

As preferred examples of R^1R^2N or $R^{1a}R^2N$ comprising R1, R^2 and the vicinal nitrogen or R^{1a}, R^2 and the vicinal nitrogen there are mentioned unsubstituted amino groups, mono-C_{1-4} alkyl amino groups such as methylamino, ethylamino and propylamino, and di-C_{1-4} alkylamino groups such as dimethylamino and ethylmethylamino. In the case of $R^{1a}R^2N$, also preferred are acylamino groups such as formylamino and acetylamino, and N-C_{1-2} acyl-N-C_{1-4} alkylamino groups such as N-formyl-N-methylamino and N-acetyl-N-methylamino. Preferred examples of R^3 and R^{3a} are hydrogen and C_{1-4} alkyl groups such as methyl, ethyl and propyl. Formyl and acetyl groups are also preferred examples of R^{3a}.

In the foregoing formula, B represents a substituted or unsubstituted homocyclic or heterocyclic group. The homocyclic or heterocyclic group of B is a cyclic group containing only the same atoms, or a cyclic group containing two or more different kinds of atoms, and means a cyclic hydrocarbon radical or a heterocyclic group. The cyclic hydrocarbon group of B include C_{3-8} cycloalkyl groups such as cyclopropyl, cyclobutyl, cyclopentyl, and cyclohexyl; C_{3-8} cycloalkenyl groups such as cyclopropenyl, 1-cyclopentenyl, 1-cyclohexenyl, 2-cyclohexenyl, and 1,3-cyclohexadienyl; and C_{6-14} aryl groups such as phenyl, 1- or 2-naphthyl, 1-, 2- or 9-anthryl, 1-, 2-, 3-, 4- or 9-phenanthryl, and 1-, 2-, 4-, 5- or 6-azulenyl. Preferred cyclic hydrocarbon radicals are aromatic, examples of which include C_{6-14} aryl groups such as phenyl. As the heterocyclic group of B there is used a five- to eight-membered ring group containing 1 to 5 hetero atoms such as oxygen, sulfur and nitrogen atoms, or a fused ring group thereof selected from 2- or 3-thienyl, 2- or 3-furyl, 2- or 3-pyrrolyl, 2-, 3- or 4-pyridyl, 2-, 4- or 5-oxazolyl, 2-, 4- or 5-thiazolyl, 3-, 4- or 5-pyrazolyl, 2-, 4- or 5-imidazolyl, 3-, 4- or 5-isoxazolyl, 3-, 4- or 5-isothiazolyl, 3- or 5-(1,2,4-oxadiazolyl), 1,3,4-oxadiazolyl, 3- or 5-(1,2,4-thiadiazolyl), 1,3,4-thiadiazolyl, 4- or 5-(1,2, 3-thiadiazolyl), 1,2,5-thiadiazolyl, 1,2,3-triazolyl, 1,2,4-triazolyl, 1H- or 2H-tetrazolyl, N-oxide-2-, 3- or 4-pyridyl, 2-, 4- or 5-pyrimidinyl, N-oxide-2-, 4- or 5-pyrimidinyl, 3- or 4-pyridazinyl, pyrazinyl, N-oxide-2- or 3-pyrazinyl, N-oxide-3- or 4-pyridazinyl, benzofuryl, benzothienyl, benzothiazolyl, benzoxazolyl, triazinyl, oxo-triazinyl, tetrazolo [1,5-b]pyridazinyl, triazolo[4,5-b]pyridazinyl, oxo-imidazolyl, dioxo-triazinyl, pyrrolidinyl, piperidyl, pyranyl, thiopyranyl, 1,4-oxazinyl, morpholinyl, 1,4-thiazinyl, 1,3-thiazinyl, piperazinyl, benzoimidazolyl, quinolyl, isoquinolyl, cinnolinyl, phthalazinyl, quinazolinyl, quinoxalinyl, indolizinyl, quinolizinyl, 1,8-naphthyridinyl, purinyl, pteridinyl, dibenzofuranyl, carbazolyl, acridinyl, phenanthridinyl, phenazinyl, phenothiazinyl, and phenoxazinyl. Five- or six-membered, nitrogen-containing heterocyclic groups such as 2-, 3- or 4-pyridyl and 2-, 4- or 5-thiazolyl are preferred. These homocyclic or heterocyclic groups may have 1 to 5 (preferably 1) substituent groups which are the same or different. Examples of such substituent groups are those referred to above in connection with the substituent R.

Preferred examples of B are five- or six-membered, nitrogen-containing heterocyclic groups such as pyridyl and thiazolyl which may be substituted with one or two halogens.

The starting compound [II] used in the present invention can be prepared easily, for example by the process described in "Journal of American Chemical Society," Vol. 76, p.1877, (1954), or a process similar thereto.

The reaction for deriving the compound [I] of the present invention from the compound [II] can be attained by the reaction of the compounds [II] and [III]. This reaction can be carried out using a suitable solvent. The solvent is not specially limited if only it does not afford a by-product through the reaction thereof with reaction substrate, reagent and product. But it is desirable to use a solvent which dissolves both reaction substrate and reagent. Examples of such solvent are aromatic hydrocarbons such as benzene, toluene and xylene; esters such as methyl acetate, ethyl acetate, ethyl formate, and ethyl propionate; ketones such as acetone and methyl ethyl ketone; ethers such as diethyl ether, dipropyl ether, dibutyl ether, tetrahydrofuran, and dioxane; nitriles such as acetonitrile and propionitrile; acid amides such as dimethyl formamide and dimethyl acetamide; sulfoxides such as dimethyl sulfoxide; sulfones such as sulforan; phosphoric acid amides such as hexamethyl phosphoramide; halogenated hydrocarbons such as dichloromethane, chloroform, 1,2-dichloroethane, and carbon tetrachloride; aromatic amines such as pyridine, picoline, lutidine, and quinoline; as well as mixtures thereof and mixtures thereof with water. Particularly preferred are pyridines such as pyridine, α-picoline, and 2,6-lutidine; nitriles such as acetonitrile; and halogenated hydrocarbons such as chloroform and dichloromethane.

For the purpose of accelerating the reaction or reducing the formation of by-product, the reaction may be performed in the presence of a base, or a base may be allowed to act before or after the reaction. As examples of the base, mention may be made of sodium hydride, sodium, alkali metal alcoholates such as sodium ethylate, sodium methylate, and potassium tert-butoxide, organic bases such as triethylamine, diisopropylethylamine, pyridine, and N,N-dimethylaniline, and inorganic bases such as potassium carbonate, sodium carbonate, sodium hydroxide, potassium hydroxide, sodium hydrogencarbonate, and potassium hydrogencarbonate. The amount of the base used is not specially limited if only it does not exert a bad influence on the reaction. For example, in the case of pyridine, it can be used in a large excess amount for serving as both base and solvent.

The amount of the compound [III] used as a reagent is in the range of 1 to 5 moles, preferably 1 to 2.5 moles, per mole of the compound [II].

The reaction temperature is usually in the range of -50° to 200°C, preferably -30° to 50°C. The reaction time is usually in the range of 0.1 to 24 hours, preferably 0.1 to 10 hours. The compound [I] obtained may be used as a starting material in the next reaction after isolation and purification by means known per se such as, for example, concentration vacuum concentration, redistribution, change of basicity, extraction with solvent , distillation, crystallization, recrystallization, or chromatography, or directly as the reaction mixture.

The di(thio)carboxylic acid derivative (III] used in the above process is in many cases a known compound. But, if necessary, it can be prepared by any of the methods described in "The chemistry of acid derivatives, part 1," JOHN WILEY & SONS (1979), Chapter 7; "The chemistry of acid derivatives, part 2," JOHN WILEY & SONS (1979), Chapter 11; and "The chemistry of acyl halides," JOHN WILEY & SONS (1972), Chapter 2, or a method similar thereto.

The reactions [I]→[V] and [I]→[VII] can be attained by reacting the compound [I] with an amine [IV] or a salt thereof or a cyclic amino compound [VI] or a salt thereof. These reactions can be carried out using a suitable solvent. The solvent is not specially limited if only it does not afford a by-product through the reaction thereof with reaction substrate, reagent and product. It is desirable to use a solvent which dissolves both reaction substrate and reagent. Examples of such solvent include aliphatic hydrocarbons such as pentane, hexane, heptane, petroleum ether; aromatic hydrocarbons such as benzene, toluene, and xylene; esters such as methyl acetate, ethyl acetate, ethyl formate, and ethyl propionate; ketones such as acetone and methyl ethyl ketone; ethers such as diethyl ether, dipropyl ether, dibutyl ether, tetrahydrofuran, and dioxane; alcohols such as methanol, ethanol, propanol, and butanol; nitriles such as acetonitrile and propionitrile; acid amides such as dimethylformamide and dimethylacetamide; sulfoxides such as dimethyl sulfoxide; sulfones such as sulforane; phosphoric acid amides such as hexamethylphosphoramide; halogenated hydrocarbons such as dichloromethane, chloroform, 1,2-dichloroethane, and carbon tetrachloride; aromatic amines such as pyridine, picoline; lutidine, and quinoline; as well as mixtures thereof and mixtures thereof with water.

The compound [IV] or a salt thereof or the compound [VI] or a salt thereof, as a reagent, can be used in an amount of 1 to 2 moles per mole of the compound [I]. But if the compound [IV] or a salt thereof is used in an excess amount, a bisamino derivative may be by-produced, so it is desirable to use it in an amount of 1 to 1.3 moles per mole of the compound [I]. The reaction temperature is usually in the range of -50° to 100°C, preferably -30° to 50°C, and the reaction time is usually in the range of 0.1 to 24 hours, preferably 0.1 to 10 hours. The resulting compound [V] or salt thereof or compound [VII] or salt thereof may be used as a starting material in the next reaction after isolation and purification by means known per se, e.g. concentration, vacuum concentration, redistribution, change of basicity, extraction with solvent , distillation, crystallization, recrystallization, or chromatography, or directly as the reaction mixture.

The amine [IV] or a salt thereof used in the above process can be prepared, for example by the method described in "Survey of Organic Synthesis," Wiley-Interscience (1970), Chapter 8, or a method similar thereto. And the cyclic amino compound [VI] or a salt thereof can be prepared, for example by the method described in "Organic Functional Group Preparations," Academic Press, Vol.1, Chapter 13 (1968), and Vol.3, Chapter 10(1972), or by the method described in Japanese Patent Laid Open No.171/1990, or a method similar thereto.

The reactions [V]→[VIII] and [VII]→[IX] can be attained by reacting the compound [V] or [VII] with [IV] or [VI] after acylation if necessary when R^1 and R^3 in the compound [V] or [VII] each represent a hydrogen atom. As a reagent in such acylation reaction there is used a known formylating agent such as, for example, formic acid, acetic formic anhydride, or formylimidazole, a known acetylating agent such as, for example, acetyl chloride or acetic anhydride, or other acylating agents.

The reactions in question can be conducted using a suitable solvent. The solvent is not specially limited if only it does not afford a by-product through the reaction thereof with reaction substrate, reagent and product. But a solvent which dissolves both reaction substrate and reagent is preferred. Examples of such solvent include aromatic hydrocarbons such as benzene, toluene, and xylene; esters such as methyl acetate, ethyl acetate, ethyl formate, and ethyl propionate; ketones such as acetone and methyl ethyl ketone; ethers such as diethyl ether, dipropyl ether, dibutyl ether, tetrahydrofuran, and dioxane; nitriles such as acetonitrile and propionitrile; acid amides such as dimethylformamide and dimethylacetamide; sulfoxides such as dimethyl sulfoxide; sulfones such as sulforane; phosphoric acid amides such as hexamethylphosphoramide; halogenated hydrocarbons such as dichloromethane, chloroform, 1,2-dichloroethane, and carbon tetrachloride; aromatic amines such as pyridine, picoline, lutidine, and quinoline; as well as mixtures thereof and mixtures thereof with water. Particularly preferred are pyridines such as pyridine, α-picoline, and 2,6-lutidine; nitriles such as acetonitrile; and halogenated hydrocarbons such as chloroform and dichloromethane.

With a view to accelerating the reaction or reducing the formation of by-product, the reaction may be performed in the presence of a base, or a base may be allowed to act before or after the reaction. As examples of the base there are mentioned alkali metal alcoholates such as sodium ethylate, sodium methylate, and potassium tert-butoxide; organic bases such as triethylamine, diisopropylethylamine, pyridine, and N,N-dimethylaniline; and inorganic bases such as potassium carbonate, sodium carbonate, sodium hydroxide, potassium hydroxide, sodium hydrogencarbonate, and potassium hydrogencarbonate. The amount of the base used is not specially limited if only it does not badly influence the reaction. For example, in the case of pyridine, it can be used in a large excess amount for serving as both base and

solvent.

The amount of the acylating agent used in the reaction is in the range of 1 to 5 moles, preferably 1 to 2.5 moles, per mole of the compound [V] or [VII].

The reaction temperature is usually in the range of -50° to 200°C, preferably -30° to 50°C, and the reaction time is usually in the range of 0.1 to 24 hours, preferably 0.1 to 10 hours. The resulting compound may be used as a starting material in the next reaction after isolation and purification by means known per se, e.g. concentration, vacuum concentration, redistribution, change of basicity, extraction with solvent, distillation, crystallization, recrystallization, or chromatography, or directly as the reaction mixture.

In the reaction [V]→[VIII], as examples of RS in the compound [V] or a salt thereof, C_{1-4} alkylthio groups such as methylthio, and C_{7-10} aralkylthio groups such as benzylthio, are particularly preferred. It is preferable that the compound [VI] or a salt thereof be used in an amount of about 0.8 to 2.0 equivalents based on the amount of the compound [V] or a salt thereof. But the compound [VI] or a salt thereof may be used in an amount of about 2.0 to 20 equivalents if this amount does not impede the reaction.

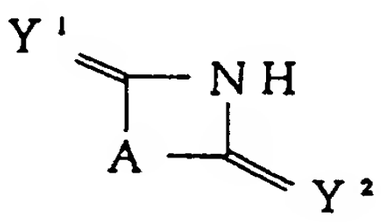
The reaction may be performed in the absence of solvent, but usually the reaction is carried out in a suitable solvent. Examples of such solvent include water, alcohols such as methanol, ethanol, n-propanol, and isopropanol; aromatic hydrocarbons such as benzene, toluene, and xylene; halogenated hydrocarbons such as dichloromethane and chloroform; saturated hydrocarbons such as hexane, heptane, and cyclohexane; ethers such as diethyl ether, tetrahydrofuran, and dioxane; ketones such as acetone; nitriles such as acetonitrile; sulfoxides such as diemthyl sulfoxide; acid amides such as N,N-dimethylformamide; esters such as ethyl acetate; and carboxylic acids such as acetic acid and propionic acid. These solvents may be used each alone or, if necessary, may be used as a mixture of two or more kinds in a suitable ratio, for example in the range of 1:1 to 1:10. In the case where the reaction mixture is not a homogeneous phase mixture, the reaction may be carried out in the presence of an inter-phase transfer catalyst such as a quaternary ammonium salt, e.g. triethylbenzylammonium chloride, tri-n-octylmethylammonium chloride, trimethyldecylammonium chloride, or tetramethylammonium bromide, or a crown ether.

This reaction may be accelerated by the addition of a base or a metallic salt in an amount of 0.01 to 10 equivalents, preferably 0.1 to 3 equivalents. As examples of such base there are mentioned inorganic bases such as sodium hydrogencarbonate, potassium hydrogencarbonate, sodium carbonate, potassium carbonate, sodium hydroxide, potassium hydroxide, calcium hydroxide, phenyllithium, butyllithium, sodium hydride, potassium hydride, sodium methoxide, sodium ethoxide, metal sodium, and metal potassium, as well as organic bases such as triethylamine, tributylamine, N,N-dimethylaniline, pyridine, lutidine, collidine, 4-(dimethylamino)pyridine, and DBU(1,8-diazabicyclo[5,4,0]undecene-7). These organic bases per se can also be used as solvents. Examples of employable metallic salts include copper salts such as copper chloride, copper bromide, copper acetate, and copper sulfate, as well as mercury salts such as mercury chloride, mercury nitrate, and mercury acetate.

In this reaction, the reaction temperature is usually in the range of -20° to 150°C and the reaction time is usually in the range of 10 minutes to 50 hours, but preferably 0° to 100°C and 1 to 20 hours, respectively.

In the reaction [VII]→[IX], preferred examples of RS and reaction conditions are the same as those mentioned in connection with the reaction [V]→[VIII].

In each of the reactions [I]→[V] and [I]→[VII] there is by-produced an imide compound represented by the following formula:



In many cases, the compound [V] or [VII] and the imide compound can be separated from each other by a known means, e.g. chromatography. But if the separation is difficult, it is possible to separate the two by using a method wherein the reaction mixture is dissolved in a basic aqueous solution and the compound [V] or [VII] and the imide compound are subjected to fractional precipitation while neutralization is allowed to proceed little by little by using an acid, or by adopting a method wherein the imide compound is decomposed into, for example, di(thio) carboxylic acid monoamide derivative by stirring in a basic aqueous solution, followed by neutralization with an acid to precipitate [V] or [VII]. As examples of bases employable in these separation methods there are mentioned inorganic bases such as sodium carbonate, potassium carbonate, sodium hydroxide, potassium hydroxide, and calcium hydroxide, as well as organic bases such as triethylamine, tributylamine, N,N-dimethylaniline, pyridine, lutidine, collidine, 4-(dimethylamino)pyridine, and DBU(1,8-diazabicyclo[5,4,0]undecene-7). Examples of the acid used for neutralization in the above methods include inorganic acids such as hydrochloric acid, hydrobromic acid, hydriodic acid, phosphoric acid, sulfuric acid, and perchloric acid, as well as organic acids such as formic acid, acetic acid, tartaric acid, malic acid, citric acid, oxalic acid,

succinic acid, beznoic acid, picric acid, and p-toluenesulfonic acid.

The above separation methods may each be used as a separation method for the compound [VIII] or [IX] and the imide compound after completion of such two-step reaction as [I]→[V]→[VIII] or [I]→[VII]→[IX].

The resulting compound [VIII] or [IX] or a salt thereof can be isolated and or purified by means known per se, e.g. concentration, vacuum concentration, redistribution, change of basicity, extraction with solvent, crystallization, recrystallization, or chromatography.

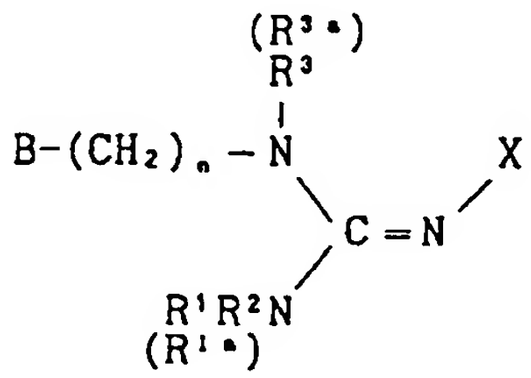
As the case may be, the compounds [I] and/or [V] and/or [VI] and/or [VII] can be converted into the desired products [VIII] and/or [IX] after transient isolation, or in situ. The compounds [VIII] and/or [IX] may be prepared via the compound [I] from the starting compounds [II] and [III] without the purification and/or isolation of the intermediates.

In the case where the resulting guanidine derivative [VIII] or [IX] is obtained as a free compound, this compound can be converted by a conventional method into a salt thereof with an inorganic acid such as, for example, hydrochloric acid, hydrobromic acid, hydriodic acid, phosphoric acid, sulfuric acid, or perchloric acid, or an organic acid such as, for example, formic acid, acetic acid, tartaric acid, malic acid, citric acid, oxalic acid, succinic acid, benzoic acid, picric acid, or p-toluenesulfonic acid.

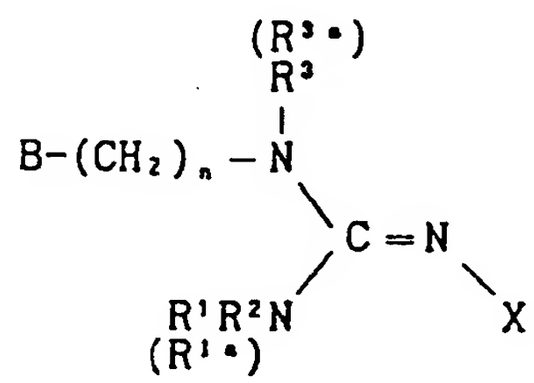
In the case where R^3 (or R^{3a})is hydrogen and R^1 (or R^{1a}) or R^2 is hydrogen, the compound in question can be converted by a conventional method into a metallic salt thereof such as, for example, sodium salt, potassium salt, or lithium salt, or an organic base such as, for example, triethylammonium salt or tetrabutylammonium salt.

In the case where the guanidine derivative is obtained in the form of a salt, it can be converted into a free compound by a conventional method. As salts of the compounds [IV], [V], [VI] and [VII] there may be used such salts as mentioned above in connection with [VIII] or [IX].

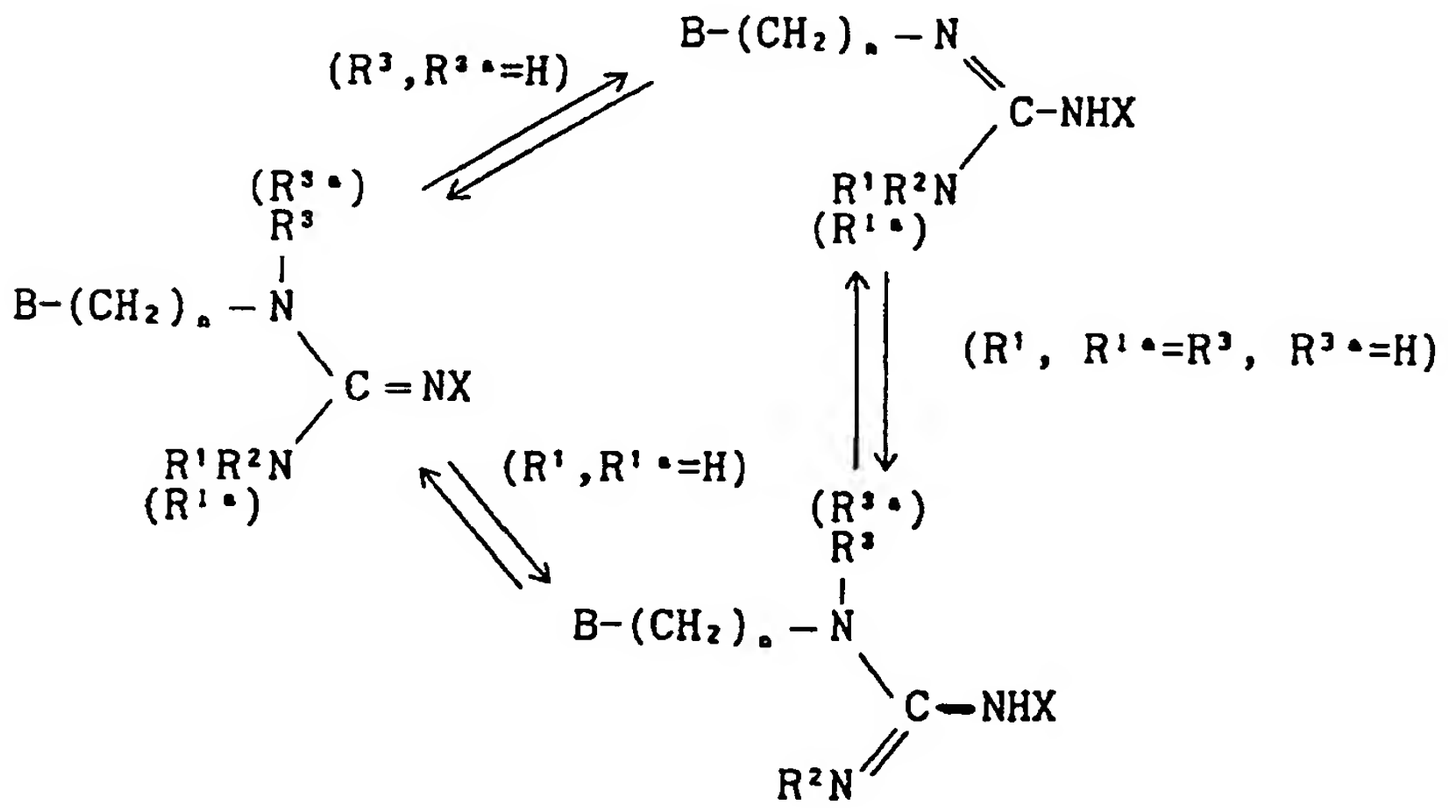
In the guanidine derivative [VIII] or [IX] or a salt thereof, there are formed stereoisomers of cis and trans forms with respect to the position of the substituent X, while when R^3 (or R^{3a}) is hydrogen and when R^1 (or R^{1a}) or R^2 is hydrogen, there are formed tautomers theoretically. These isomers are all included in the compound [VIII] or [IX] or a salt thereof according to the present invention.



(cis)-[VIII], [IX]



(trans)-[VIII], [IX]



The guanidine derivative [VIII] or [IX] and salts thereof are effective in the control of sanitary insect pests and ani-

mal/plant parasitic insects, and exhibit a strong insecticidal action when contacted directly with insects, for example by being sprinkled directly over animals and plants with insect pests parasitic thereon. But a more characteristic point resides in that they exhibit a strong insecticidal action also when they are once absorbed into a plant through the root, leaves, or stalk of the plant and thereafter an insect pest sucks or chews the plant or comes into contact with the plant. This property is advantageous in exterminating sucking or chewing insect pests. Besides, the compounds [VIII], [IX] and salts thereof are low in chemical injury against plants and also low in toxicity against fish. Thus, they possess safe and advantageous properties as insect pest control agents for sanitation, horticulture, particularly for agriculture.

Examples

Working examples of the present invention will be given below to illustrate the invention in more detail.

In the Working Examples and Reference Example, the elution in column chromatography was performed under observation using TLC (Thin Layer Chromatography). In the TLC observation, Kiesel gel $60F_{254}$ (70-230 mesh, a product of Merck Co.) was used as a TLC plate; the solvent used as an eluant in column chromatography was used as a developing solvent; and a UV detector was used for detection. Further, as a silica gel for column chromatography there was used Kieselgel 60 (70-230 mesh, a product of Merck Co.). NMR spectrum represents proton NMR, there was used tetramethylsilane as an internal reference standard, measurement was made using a VARIAN EM390 (90MHz) type or Hitachi R-600 (60 MHz) type spectrometer, and all δ values were shown in terms of parts per million (ppm). Each parenthesized value in the case of using a mixed solvent as a developing solvent represents a volume ratio of the ingredients thereof.

The abbreviations used in the following Examples and Table-1 have the following meanings.

Me: methyl, Et: ethyl, Ph: phenyl, s: singlet, br: broad, d: doublet, t: triplet, q: quartet, m: multiplet, dd: doublet of doublets, J: coupling constant, Hz: hertz, $CDCl_3$:deuteriochlorofrom, DMSO-d_6: deuteriodimethylsulfoxide, %: wt%, mp: melting point. "Room temperature" indicates about 15-25°C.

Example 1

A mixture consisting of 5 g S-methyl-N-nitroisothiourea and 70 ml pyridine was ice-cooled, into which was then added 14.5 g of phthaloyl chloride dropwise over a period of 30 minutes. After stirring for 10 minutes under ice-cooling, the reaction mixture was poured into an ice-cooled, diluted hydrochloric acid (concentrated hydrochloric acid 100 ml, water 500 ml) and the resulting crystals were collected by filtration. Then, 50 ml of EtOH was added for recrystallization to afford 8.0 g of S-methyl-N-nitro-N'-Phthaloylisothiourea as white needle-like crystals, mp 138-140°C.

^{1}H-NMR($CDCl_3$): 8.10-7.80 (4H, m), 2.64 (3H, s)

Example 2

A mixture consisting of 2 g S-methyl-N-nitro-N'-phthaloylisothiourea and 20 ml acetonitrile was ice-cooled, into which was then added 1.1 g of 2-chloro-5-(aminomethyl)thiazole dropwise over a 10 minute period. After stirring for 30 minutes under ice-cooling, the reaction mixture was concentrated and the residue was purified by column chromatography [eluent: chloroform-ethanol (20:1)] to afford 1.93 g of N-(2-chloro-5-thiazolylmethyl)-S-methyl-N'-nitroisothiourea as a light yellow powder, mp 162.5-165°C.

^{1}H-NMR(DMSO-d_6): 9.20-8.60 (1H, br), 7.53 (1H, s), 4.72 (2H, d, J=5.0Hz), 2.44 (3H, s)

Example 3

A mixture consisting of 300 mg S-methyl-N-nitro-N'-phthaloylisothiourea and 10 ml acetonitrile was ice-cooled, into which was then added 150 mg of benzylamine dropwise over a 10 minute period. After stirring for 15 minutes under ice-cooling, the reaction mixture was concentrated and the residue was purified by column chromatography [eluent: n-hexane-ethyl acetate (1:1)] to afford 248 mg of N-benzyl-S-methyl-N'-nitroisothiourea as a white powder, mp 77-80 °C.

^{1}H-NMR(DMSO-d_6): 10.20-8.20 (1H, br), 7.32 (4H, s), 4.64 (2H, S), 2.46 (3H, s)

Example 4

349 mg of a 40% methylamine methanol solution was dropwise added to a mixture consisting of 1 g N-(2-chloro-5-thiazolylmethyl)-S-methyl-N'-nitroisothiourea and 30 ml acetonitrile, at room temperature, over 5 minutes. After stirring for 1.5 hours, the resultant white precipitate was collected by filtration and then dried to afford 410 mg of N-(2-chloro-5-

thiazolylmethyl)-N'-methyl-N''-nitroguanidine (compound No. 14) as a white powder. The mother liquor after the filtration was concentrated, then 20 ml of ethanol was added, followed by stirring thoroughly, and the crystals formed were collected by filtration to obtain additional 330 mg of compound No.14 (mp 172-173°C). Upon recrystallization from acetonitrile, this product exhibited mp 173-174°C.

^{1}H-NMR(DMSO-d_6): 9.15-8.75 (1H, br), 7.58 (1H, s), 8.25-7.90 (1H, br), 4.51 (2H, d, J=5.0Hz), 2.84 (3H, d, J=5.0Hz)

Example 5

A mixture consisting of 10 g S-methyl-N-nitro-N'-phthaloylisothiourea and 100 ml acetonitrile was ice-cooled, into which was then added 5.6 g of 2-chloro-5-(aminomethyl) thiazole dropwise over a 10 minute period. After stirring for 30 minutes under ice-cooling, the temperature was raised to room temperature, and 3.5 g of a 40% methylamine methanol solution was dropwise added over 5 minutes. After stirring for 1.5 hours, the reaction mixture was concentrated to afford 14.9 g of a mixture consisting of N-(2-chloro-5-thiazolylmethyl)-N'-methyl-N''-nitroguanidine (compound No.14) and phthalimide, as a white powder. This white powder was dissolved in an aqueous potassium hydroxide solution (potassium hydroxide 8.5 g, water 80 ml). Subsequent 1 hour stirring at room temperature was followed by ice-cooling, and then 8 ml of concentrated hydrochloric acid was added little by little. After stirring for another 30 minutes under ice-cooling, the resultant crystals were collected by filtration and dried to give 8.8 g of compound No.14 as a light yellow powder. This product was the same in melting point, NMR, IR and TLC Rf values as the compound obtained in Example 4.

Example 6

252 mg of a 50% aqueous dimethylamine solution was dropwise added to a mixture consisting of 600 mg N-(2-chloro-5-thiazolylmethyl)-S-methyl-N'-nitroisothiourea and 20 ml acetonitrile at room temperature. After stirring at room temperature for 2 hours,the reaction mixture was concentrated and 20 ml of ethanol was added to the residue, followed by stirring thoroughly. The resultant crystals were collected by filtration and dried to afford 350 mg of N-(2-chloro-5-thiazolylmethyl)-N',N'-dimethyl-N''-nitroguanidine (compound No.17) as a white powder. The mothor liquor after the filtration was concentrated and 5 ml of ethanol was added, followed by stirring thoroughly, then the resultant crystals were collected by filtration and dried to give additional 120 mg of compound No.17 (mp 154-159°C). Recrystallization of this product from acetonitrile afforded a product having a melting point of 164-166°C.

^{1}H-NMR(DMSO-d_6): 8.70-8.35 (1H, br), 7.51 (1H, s), 4.53 (2H, br), 3.00 (6H, s)

Example 7

A mixture consisting of 0.5 g S-methyl-N-nitroisothiourea, 1.5 g potassium carbonate and 30 ml acetonitrile was ice-cooled and 1.5 g of succinic acid chloride was added to the ice-cooled mixture dropwise over 2 minutes. After stirring for 1 hour under ice-cooling, there was made stirring for additional 30 minutes at room temperature. Insolubles were filtered off and thereafter the solvent was distilled off, while the residue was dissolved in chloroform, washed with aqueous sodium bicarbonate, then dried over anhydrous magnesium sulfate and concentrated. The residue was purified by column chromatography [eluent: chloroform-ethanol (10:1)] to give 0.28 g of S-methyl-N-nitro-N'-succinylisothiourea as a white powder, mp 114-115°c.

^{1}H-NMR($CDCl_3$): 2.90 (4H, s), 2.60 (3H, s)

Example 8

A mixture consisting of 210 mg S-methyl-N-nitro-N'-succinylisothiourea and 10 ml acetonitrile was ice-cooled and 160 mg of 2-chloro-5-(aminomethyl)thiazole was added to the ice-cooled mixture over 30 seconds. After stirring for 10 minutes under ice-cooling, the solvent was distilled off and the residue was washed with 12 ml of water, then the resultant crystals were collected by filtration and air-dried to give 220 mg of N-(2-chloro-5-thiazolylmethyl)-S -methyl-N'-nitroisothiourea as a yellow powder. This product was the same in melting point, NMR, IR and TLC Rf values as the compound obtained in Example 2.

Example 9

A mixture consisting of 0.5 g S-methyl-N-nitroisothiourea, 1.03 g potassium carbonate and 10 ml acetonitrile was ice-cooled and 1.65 g of glutaric acid chloride was added to the ice-cooled mixture dropwise over 2 minutes. After stir-

ring for 1 hour under ice-cooling, there was made stirring for another 1 hour at room temperature. Insolubles were filtered off and the solvent was distilled off, then the residue was purified by column chromatography [eluent: chloroform-ethanol (10:1)] to give 0.22 g of N-glutaryl-S-methyl-N'-nitroisothiourea as a white powder, mp 147-149°C.

^{1}H-NMR($CDCl_3$): 2.70 (t, 4H), 2.60 (s, 3H), 1.70-2.30 (m, 2H)

Example 10

A mixture consisting of 0.18 g N-glutaryl-S-methyl-N'-nitroisothiourea and 10 ml acetonitrile was ice-cooled and 0.1 g of 2-chloro-5-(aminomethyl)thiazole was dropwise added to the ice-cooled mixture. After stirring for 30 minutes under ice-cooling, there was made stirring for additional 1 hour at room temperature. The solvent was distilled off and then the residue was purified by column chromatography [eluent: chloroform-ethanol (10:1)] to yield 170 mg of N-(2-chloro-5-thiazolylmethyl)-S-methyl-N'-nitro-isothiourea as a white powder. This product was the same in melting point, NMR, IR and TLC Rf values as the compound obtained in Example 2.

Example 11

A mixture consisting of 0.5 g S-methyl-N-nitroisothiourea, 2.06 g potassium carbonate, 30 ml acetonitrile and 1 ml water was ice-cooled and 1.55 g of cis-1,2-cyclohexanedicarboxylic acid chloride was dropwise added to the ice-cooled mixture over 1 minute. After stirring for 20 minutes under ice-cooling, there was made stirring for additional 1 hour at room temperature. Then, 30 ml of water and 30 ml of chloroform were added to the reaction mixture for separation into layers. The resultant aqueous layer was extracted using 100 ml of chloroform, while organic layers were combined together, dried and then concentrated. The residue was purified by column chromatography [eluent: chloroform-ethanol (10:1)] to yield 270 mg of N-(cyclohexane-cis-1,2-dicarbonyl)-S-methyl-N'-nitroisothiourea as a white powder, mp 112-113°C.

^{1}H-NMR($CDCl_3$): 2.90-3.20 (m, 2H), 2.60 (s, 3H), 1.30-2.10 (m, 8H)

Example 12

A mixture consisting of 370 mg N-(cyclohexane-cis-1,2-dicarbonyl)-S-methyl-N'-nitroisothiourea and 10 ml acetonitrile was ice-cooled and 223 mg of 2-chloro-5-(aminomethyl)thiazole was dropwise added to the ice-cooled mixture. After stirring for 30 minutes under ice-cooling, there was made stirring for additional 1 hour at room temperature. The solvent was distilled off and the residue was purified by column chromatography [eluent: chloroform-ethanol (10:1)] to afford 170 mg of N-(2-chloro-5-thiazolylmethyl)-S-methyl-N'-nitroisothiourea as a white powder. This product was the same in melting point, NMR, IR and TLC Rf values as the compound obtained in Example 2.

Example 13

A mixture of 0.5 g S-methyl-N-nitroisothiourea and 20 ml pyridine was heated to 62°C and a solution of 1.27 g diglycolic acid dichloride in 2 ml acetonitrile was added to the ice-cooled mixture dropwise over 1 minute. After heating and stirring for 80 minutes, the reaction mixture was added into dilute hydrochloric acid (concentrated hydrochloric acid 50 ml, water 50 ml, ice 20g) and extracted using 90 ml of chloroform. The chloroform layer was washed with 30 ml of aqueous sodium bicarbonate, followed by drying over magnesium sulfate. Subsequent concentration afforded an oily product, to which was then added a small amount of ethyl acetate, followed by stirring. As a result, crystals were precipitated, which were then collected by filtration to yield 440 mg of S-methyl-N-nitro-N'-(2,2'-oxydiacetyl)isothiourea as white crystals, mp 132-134 °C.

^{1}H-NMR($CDCl_3$): 4.40 (s, 4H), 2.65 (s, 3H)

Example 14

A mixture consisting of 90 mg S-methyl-N-nitro-N'-(2,2'-oxydiacetyl)isothiourea and 9 ml chloroform was ice-cooled and a solution of 100 mg 2-chloro-5-(aminomethyl)thiazole in 0.5 ml chloroform was dropwise added to the ice-cooled mixture. After stirring for 20 minutes under ice-cooling and 50 minutes at room temperature, there were added 15 ml of water and 15 ml of chloroform for separation into layers. The resultant aqueous layer was extracted using 50 ml of chloroform, while the resultant organic layers were combined together, the solvent was distilled off and the residue was purified by column chromatography [eluent: chloroform-ethanol (10:1)] to afford 30 mg of N-(2-chloro-5-thiazolylmethyl)-S-methyl-N'-nitroisothiourea as a white powder. This product was the same in melting point, NMR, IR and TLC Rf values

as the compound obtained in Example 2.

Example 15 Into a mixture of 1 g S-methyl-N-nitroisothiourea, 6.15 g potassium carbonate and 100 ml acetonitrile was added dropwise 2.7 g of adipic acid dichloride over 5 minutes while the mixture was stirred at room temperature. After stirring for 2 hours, the resultant crystals were recovered by filtration and washed with a small amount of acetonitrile to give 470 mg of N-adipoyl-S-methyl-N'-nitro-isothiourea as white crystals, mp 193-194 °C.

^{1}H-NMR($CDCl_3$): 3.00-2.20 (m, 4H), 2.40 (s, 3H), 2.00-1.40 (m, 4H)

Example 16

Into a mixture of 300 mg S-methyl-N-nitro-N'-succinylisothiourea and 5 ml acetonitrile was added dropwise 236 mg of (6-chloro-3-pyridyl)methylethylamine under ice-cooling. After stirring at room temperature for 13 hours, the reaction mixture was concentrated and the residue was dissolved in 100 ml of ethyl acetate, followed by washing with two 50 ml portions of water. The resultant organic layers were concentrated to give 350 mg of N-(6-chloro-3-pyridylmethyl)-N-ethyl-S-methyl-N'-nitroisothiourea as a light brown oil.

^{1}H-NMR($CDCl_3$): 8.33(1H,br), 7.73(1H,dd,J=9.0Hz,2.5Hz), 7.36(1H,d,J=9.0Hz), 4.83(2H,s), 3.65(2H,q), 2.57(3H,s), 1.29(3H,t)

Example 17

(6-Chloro-3-pyridyl)methylamine (197 mg) was dropwise added under ice-cooling into a mixture consisting of 300 mg S-methyl-N-nitro-N'-succinylisothiourea and 5 ml acetonitrile. After stirring for 1 hour under ice-cooling, the reaction mixture was concentrated and 30 ml of water was added to the residue, followed by stirring thoroughly. The resultant crystals were collected by filtration and dried to yield 360 mg of N-(6-chloro-3-pyridylmethyl)-S-methyl-N'-nitroisothiourea, mp 140-141.5°C.

^{1}H-NMR($CDCl_3$+DMSO-d_6): 9.60-8.90 (1H,br), 8.40 (1H,br), 7.78 (1H,dd,J=9.0Hz, 2.5Hz), 7.33(1H,d,J=9.0Hz), 4.63(2H,s), 2.48 (3H,s)

Example 18

To a mixture of 1 g N-(2-chloro-5-thiazolylmethyl)-S-methyl-N'-nitroisothiourea, 560 mg potassium carbonate, 400 mg cuprous chloride and 12 ml acetonitrile was added 610 mg of 2-chloro-5-(aminomethyl)thiazole and the mixture was stirred for 1 hour under reflux. Thereafter, the reaction mixture was concentrated, then water was added to the resultant solids, followed by stirring thoroughly. Thereafter, the solids were collected by filtration and purified by column chromatography [eluent: dichloromethane-methanol (10:1)] to afford 191 mg of N,N'-bis(2-chloro-5-thiazolylmethyl)-N''-nitroguanidine (compound No.39) as a white powder, mp 217-218°C.

^{1}H-NMR(DMSO-d_6): 8.95 (2H,br), 7.59 (2H,s), 4.60(4H,br)

Example 19

A mixture consisting of 1 g N-(2-chloro-5-thiazolylmethyl)-S-methyl-N'-nitroisothiourea, 1.15 g acetic anhydride and 25 ml pyridine was stirred at room temperature for 3 hours. The reaction mixture was added into an aqueous hydrochloric acid solution (concentrated hydrochloric acid 20 ml, water 50 ml, ice 10 g) for separation into layers. The resultant aqueous layer was extracted with 120 ml of chloroform, while the resultant organic layers were combined together, dried over magnesium sulfate and concentrated to afford 1.15 g of N-acetyl-N-(2-chloro-5-thiazolylmethyl)-S-methyl-N'-nitroisothiourea as a brown crystal, mp 77-78 °C.

^{1}H-NMR($CDCl_3$): 7.50 (1H, s), 4.80 (2H, s), 2.52 (3H, s), 2.26 (3H, s)

Then, a solution of 130 mg 40% methylamine methanol solution in 3 ml chloroform was dropwise added into a mixture of 0.5 g of the compound thus prepared and 7 ml of chloroform under stirring at -15 °C. Stirring was made for 2 hours while the temperature was raised gradually, then the reaction mixture was concentrated and purified by column chromatography [eluant: chloroform-ethanol(10:1)] to afford 180 mg of N-acetyl-N-(2-chloro-5-thiazolylmethyl)-N'-methyl-N''-nitroguanidine (compound No. 38) as a white powder, mp 105-106°C.

^{1}H-NMR($CDCl_3$): 7.50 (1H, s), 4.90 (2H, s), 3.05 (3H, s), 2.25 (3H, s)

Example 20

To a mixture of S-methyl-N-nitro-N'-phthaloylisothiourea (20 g) and toluene (300 ml) was added dropwise 40% solution of methylamine in methanol at -7°C over 30 minutes. The mixture was stirred at -7°C over 30 minutes and the resulting crystals were separated by filtration and dried by air to yield 19.7 g of white crystals. The toluene filtrate was concentrated to give 2.7 g of yellow crystals. These crystals were combined and dissolved in an aqueous solution of potassium hydroxide (potassium hydroxide, 16.9 g and water, 160 ml). The solution was stirred at room temperature for 1 hour, and cooled with ice, into which was then added dropwise 16 ml of concentrated hydrochloric acid. The mixture was stirred for 10 minutes under ice-cooling and the resulting crystals were collected by filtration and dried to afford 9.8 g of N,S-dimethyl-N'-nitroisothiourea as a pale yellow powder, mp 150-152°C.

^{1}H-NMR(DMSO-d_6): 8.30-8.95 (1H, br), 2.94 (3H, s, NMe), 2.44 (3H, s, SMe)

Example 21

To a mixture of N,S-dimethyl-N'-nitroisothiourea (500 mg), potassium carbonate (695 mg) and acetonitrile (10 ml) was added 376 mg of acetic anhydride at room temperature. After stirring at room temperature for 5 hours, 10 ml of 2N hydrochloric acid was added to the mixture which was then extracted with 40 ml of dichloromethane. The resultant organic layers were washed with aqueous saturated sodium bicarbonate, then dried over anhydrous magnesium sulfate and concentrated to afford 600 mg of N-acetyl-N,S-dimethyl-N'-nitroisothiourea as a white crystal, mp 40-41°C.

^{1}H-NMR($CDCl_3$): 2.23(3H, s), 2.52 (3H, s), 3.17 (3H, s)

To a mixture of the compound thus obtained (300 mg), and dichloromethane (5 ml) was added dropwise a solution of 5-(aminomethyl)-2-chlorothiazole (241 mg) in 1 ml of dichloromethane at -10°C. After stirring at -10°C for 2 hours, 10 ml of 2N hydrochloric acid was added to the mixture. The resultant organic layers were separated by partition, dried over anhydrous magnesium sulfate and concentrated to afford 430 mg of colorless oily products. The product was dissolved in 5 ml of toluene and 5 ml of n-hexane was added to the solution before vigorously stirring. White precipitates were formed by such treatments, collected by filtration and dried to afford 260 mg of N-acetyl-N'-(2-chlorothiazolylmethyl)-N-methyl-N''-nitroguanidine as a white powder, mp 105-108°C.

^{1}H-NMR($CDCl_3$): 9.35(1H, br), 7.53 (1H, s), 4.57 (2H, s) 3.08(3H, s), 2.11 (3H, s).

Example 22

To a mixture of N-(6-chloro-3-pyridylmethyl)-S-methyl-N'-nitroisothiourea (1.3 g) and acetonitrile (10 ml) was added pyridine (1.6 g) and further dropwise acetyl chloride (0.79 g) under ice-cooling. After stirring for 1 hour under ice-cooling, the mixture was warmed to room temperature and stirred at the same temperature for 2 hours. The reaction mixture was concentrated and 50 ml of ether and 5 ml of 2N hydrochloric acid were added to the mixture which was then partitioned. The resultant organic layers were dried over anhydrous magnesium sulfate and concentrated to afford 1.6 g of N-acetyl-N-(6-chloro-3-pyridylmethyl)-S-methyl-N'-nitroisothiourea as a red oil.

^{1}H-NMR($CDCl_3$): 8.39(1H, d, J=2.0Hz), 7.72(1H, dd, J=8.0Hz, 2.0Hz), 7.31(1H, d, J=8.0Hz), 4.75 (2H, s), 2.50 (3H, s), 2.28 (3H, s).

Into a mixture of the compound thus prepared (1.6 g) and acetonitrile (10 ml) was added dropwise 0.39 g of 40% methylamine solution in methanol at -5°C. After stirring at -3°C for 30 minutes, the mixture was concentrated. The resultant yellow oil was subjected to column chromatography [eluent: chloroform-ethanol(20:1)] to afford 0.65 g of N-acetyl-N-(6-chloro-3-pyridylmethyl)-N'-methyl-N''-nitroguanidine as a white powder, mp 124-125°C.

^{1}H-NMR($CDCl_3$): 9.20 (1H, br), 8.32(1H, d, J=2.0Hz), 7.75 (1H, dd, J=2.0Hz, 8.0Hz), 7.30(1H, d, J=8.0Hz), 4.78 (2H, s), 2.98(3H, d, J=5.0Hz), 2.21(3H, s).

Reference Example 1

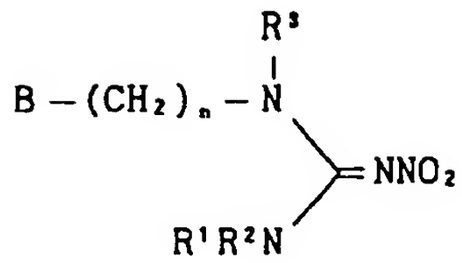
190 mg of acetic anhydride was added to a mixture consisting of 180 mg of the compound No.38 prepared in Example 19 and 5 ml of pyridine at room temperature. After stirring at room temperature for 80 minutes, the reaction mixture

was added into an aqueous hydrochloric acid solution (concentrated hydrochloric acid 20 ml, water 50 ml) for separation into layers. The resultant aqueous layer was extracted with chloroform (90 ml), while the resultant organic layers were combined together, dried over magnesium sulfate, concentrated and then purified by column chromatography [eluent: chloroform-ethanol (10:1)] to give 130 mg of N,N'-diacetyl-N-(2-chloro-5-thiazolylmethyl)-N'-methyl-N''-nitroguanidine as a white powder, mp 72-74°C.

^{1}H-NMR($CDCl_3$): 7.50(1H,s), 5.00(1H,br), 3.20(1H,br), 2.37(3H,br), 2.20(3H,br)

Table-1 below shows compounds prepared according to the process of the present invention, including those prepared in the above Examples 1-22.

Table-1



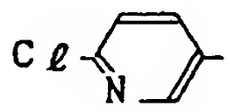
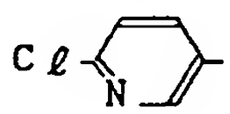
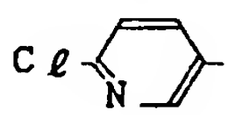
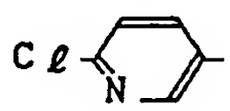
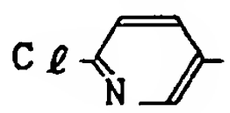
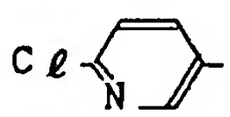
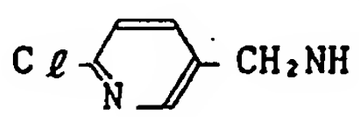
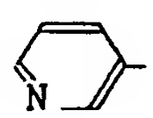
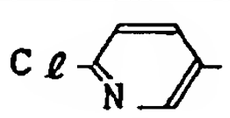
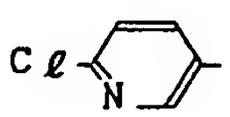
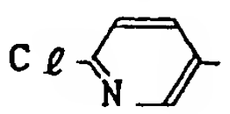
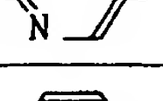
Compound No.	B	n	R^3	R^1R^2N	Mp (℃)
1		1	H	MeNH	150～152
2		1	H	Me_2N	160.5～162.5
3		1	Me	NH_2	167～170
4		1	Me	MeNH	136～137
5		1	H	EtNH	137.5～138
6		1	H		213～215.5
7		1	H	H_2N	185～190
8		1	Et	MeNH	114.5～115
9		1	Me	Me_2N	99～101
10		1	H	H_2N	195～197
11		1	Et	H_2N	137～139
12		1	H	MeNH	169～171

Table-1 (cont'd)

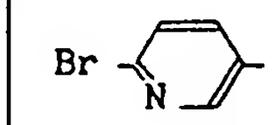
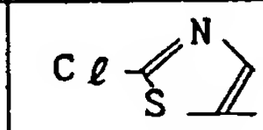
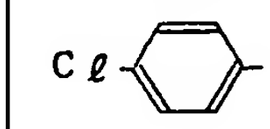
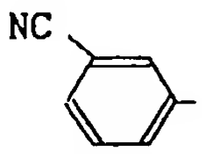
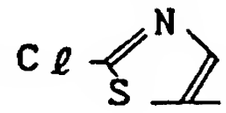
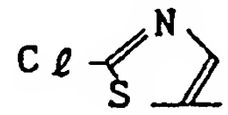
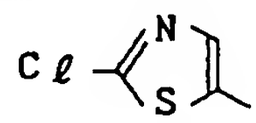
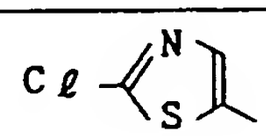
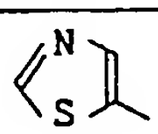
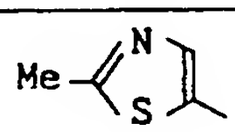
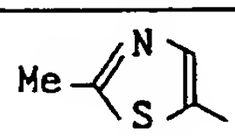
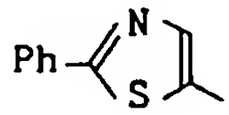
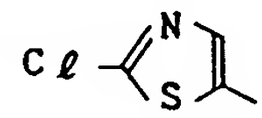
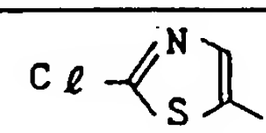
Compound No.	B	n	R^3	R^1R^2N	Mp (°C)
13		1	H	MeNH	a) amorphous
14		1	H	MeNH	173～174
15		1	H	MeNH	188～190.5
16		1	H	MeNH	133～135
17		1	H	Me_2N	164～166
18		1	Et	MeNH	b) (syrup)
19		1	Me	MeNH	c) (syrup)
20		1	Me	H_2N	121～122
21		1	H	MeNH	157～166
22		1	H	Me_2N	173～174
23		1	H	MeNH	175～179
24		1	H	MeNH	171～173
25		1	H	Et_2N	d) (syrup)
26		1	H	EtNMe	165～167

Table-1 (cont'd)

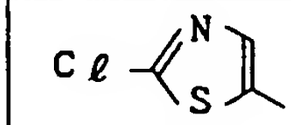
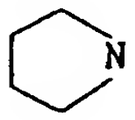
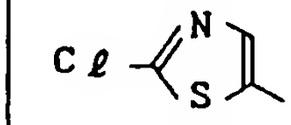
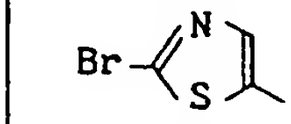
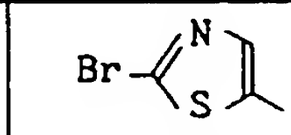
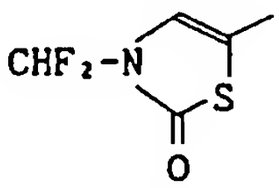
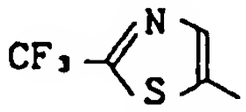
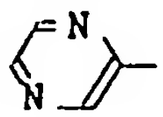
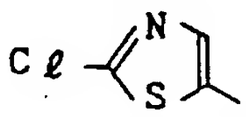
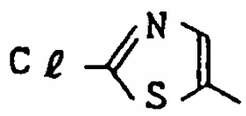
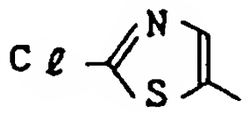
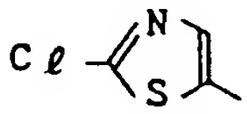
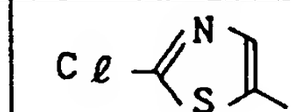
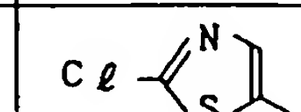
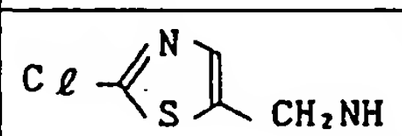
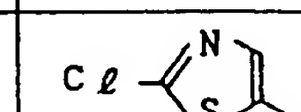
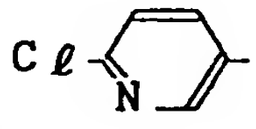
Compound No.	B	n	R^3	R^1R^2N	M.p. (°C)
27		1	H		185～188
28		1	Me	Me_2N	103～104
29		1	H	MeNH	170
30		1	H	Me_2N	185～187
31		1	H	Me_2N	(syrup) e) solidifies on standing
32		1	H	MeNH	119～121
33		1	H	MeNH	178～180
34		1	H	H_2N	162～164
35		1	Me	AcNMe	90.5～91.5
36		1	Et	Me_2N	110～111
37		1	CHO	MeNH	(syrup) f)
38		1	Ac	MeNH	105～106
39		1	H		217～218
40		1	H	AcNMe	105～108

Table-1 (cont'd)

Compound No.	B	n	R^3	R^1R^2N	Mp (℃)
4 1		1	Ac	MeNH	124～125

a) ^{1}HNMR($CDCl_3$):3.00(3H,d,J=4Hz), 4.53(2H,d,J=6Hz),
6.76(1H,br.s), 7.46(1H,d,J=8Hz),
7.67(1H,dd,J=8.3Hz), 8.20(1H,d,J=3Hz),
8.83(1H,br.s).

b) ^{1}HNMR($CDCl_3$):1.26(3H,t,J=7Hz), 2.98(3H,d,J=2Hz),
3.47(2H,q,J=7Hz), 4.70(2H,s), 7.50(1H,s),
7.96(1H,br.s).

c) ^{1}HNMR($CDCl_3$):3.00(3H,d,J=4Hz), 3.09(3H,s), 4.69(2H,s),
7.50(1H,s), 8.00(1H,br.s).

d) ^{1}HNMR($CDCl_3$):1.23(6H,t,J=7Hz), 3.46(4H,q,J=7.2Hz),
4.60(2H,br.s), 7.44(1H,s), 8.30(1H,br.s).

e) ^{1}HNMR($CDCl_3$):3.11(6H,s), 4.42(2H,d,J=6Hz), 6.86(1H,s),
7.07(1H,t,J=60Hz), 7.78(1H,br.t,J=6Hz).

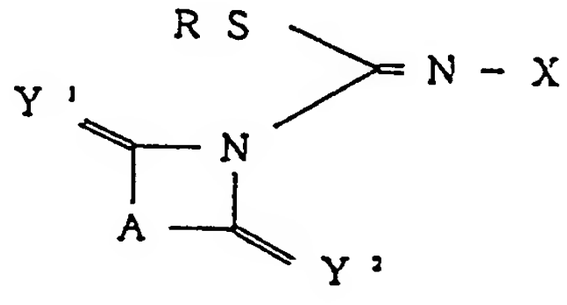
f) ^{1}HNMR(DMSO-d_6):9.70-9.00(1H,br), 8.68(1H,s), 7.55(1H,s),
4.95(2H,s), 2.93(3H,d,J=4Hz).

The present invention provides a process which is advantageous to an industrial mass production of novel guanidine derivatives or salts thereof exhibiting a superior insecticidal action.

Claims

Claims for the following Contracting States : AT, BE, CH, DE, DK, FR, GB, GR, IT, LI, LU, NL, SE

1. A compound having the following formula:



wherein

R is C_{1-10} alkyl (straight, branched or cyclic), C_{2-10} alkenyl, C_{2-10} alkynyl, C_{7-12} aralkyl, or C_{1-10} acyl (aliphatic, alicyclic, aromatic, or heterocyclic), which may be optionally substituted with one to five same or different substituents selected from

C_{3-10} cycloalkyl, C_{3-10} cycloalkenyl, C_{6-10} aryloxy, C_{6-10} arylthio, C_{6-10} arylsulfinyl, C_{6-10} arylsulfonyl, C_{6-10} arylamino, thienyl, fury], pyrazolyl, thiazolyl, isothiazolyl, oxazolyl, isoxazolyl, imidazolyl, triazolyl, tetrazolyl, pyridyl, pyrimidinyl, pyridazinyl, quinolyl, isoquinolyl, indolyl, and (in case of R being C_{7-12} aralkyl and C_{1-10} acyl) C_{6-10} aryl and C_{7-10} aralkyl,

C_{2-10} alkenyl, C_{2-10} alkynyl, C_{1-4} alkoxy, C_{1-4} alkylthio, C_{1-4} alkylsulfinyl, C_{1-4} alkylsulfonyl, amino, mono- or di-C_{1-4} alkylamino, C_{3-6} cycloalkylamino, and (in case of R being C_{7-12} aralkyl and C_{1-10} acyl) C_{1-15} alkyl,

nitro, hydroxyl, mercapto, oxo, thioxo, cyano, carbamoyl, carboxyl, C_{1-4} alkoxycarbonyl, sulfo, halogen, C_{2-6} acylamino, C_{2-4} acyl, and C_{6-10} arylcarbonyl;

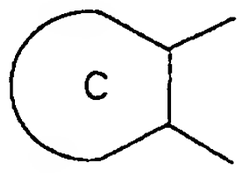
X is an electron withdrawing group selected from cyano, nitro, alkoxycarbonyl, hydroxycarbonyl, C_{6-10} aryloxycarbonyl, C_{1-4} alkylsulfonyl (optionally substituted with halogen), sulfamoyl, di-C_{1-4} alkoxyphosphoryl, C_{1-4} acyl (optionally substituted with halogen), carbamoyl, C_{1-4} alkylsulfonylthiocarbamoyl, thienyloxycarbonyl, furyloxycarbonyl, pyrazolyloxycarbonyl, thiazolyloxycarbonyl, isothiazolyloxycarbonyl, oxazolyloxycarbonyl, isoxazolyloxycarbonyl, imidazolyloxycarbonyl, triazolyloxycarbonyl, tetrazolyloxycarbonyl, pyridyloxycarbonyl, pyrimidinyloxycarbonyl, pyridazinyloxycarbonyl, quinolyloxycarbonyl, isoquinolyloxycarbonyl, and indolyloxycarbonyl;

Y^1 and Y^2, which are the same or different, are each independently oxygen or sulfur; and

A is a divalent hydrocarbon residue selected from C_{1-4} alkylene,

and a cyclic group

represented by the following formula:



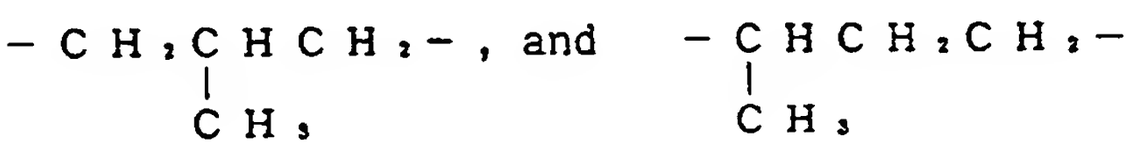
wherein the C-ring represents benzene or cyclohexane.

2. A compound according to claim 1, wherein R is C_{1-10} alkyl, or C_{7-12} aralkyl.

3. A compound according to claim 1, wherein A is C_{1-4} alkylene selected from:

$-CH_2-$, $-CH_2CH_2-$, $-CH_2CH_2CH_2-$,

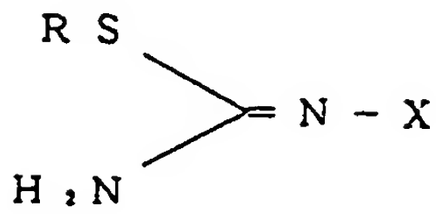
$-(CH_2)_4-$,



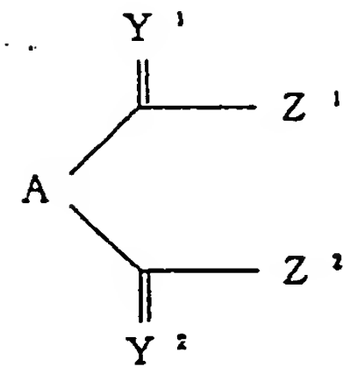
4. A compound according to claim 1, wherein A is o-phenylene, 1,2-ethylene or 1,3-propylene.

5. A compound according to claim 1, wherein said electron withdrawing group X is cyano, or nitro.

6. A process for preparing the compound of claim 1 which comprises reacting a compound of the following formula:



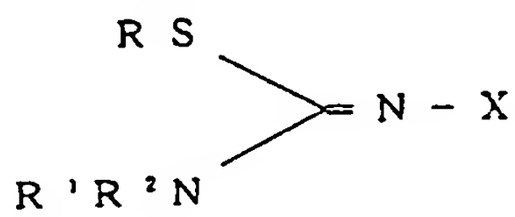
with a compound of the following formula:



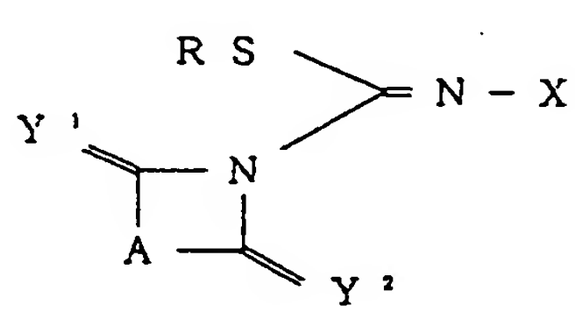
wherein

A, R, X, Y^1 and Y^2 are of the same meaning as defined in claim 1; and
Z^1 and Z^2, which are the same or different, are selected from fluorine, chlorine and bromine; or
Z^1 and Z^2 taken together represent oxygen.

7. A process for preparing a compound having the following formula, or a salt thereof:



which comprises reacting a compound of the following formula:



with a compound of the following formula:

$$R^1R^2NH$$

wherein

A, R, X, Y^1 and Y^2 are of the same meaning as defined in claim 1; and
R^1 and R^2, which are the same or different, are each independently hydrogen, C_{1-10} alkyl (straight, branched, or cyclic), C_{2-10} alkenyl, C_{2-10} alkynyl, or C_{7-12} aralkyl, which may be optionally substituted with one to five same or different substituents selected from
C_{3-10} cycloalkyl, C_{3-10} cycloalkenyl, C_{6-10} aryloxy, C_{6-10} arylthio, C_{6-10} arylsulfinyl, C_{6-10} arylsulfonyl,

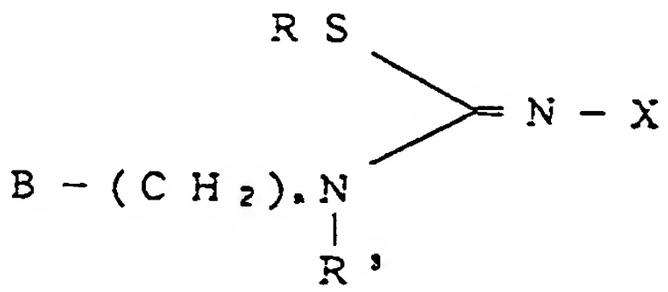
C_{6-10} arylamino, thienyl, furyl, pyrazolyl, thiazolyl, isothiazolyl, oxazolyl, isoxazolyl, imidazolyl, triazolyl, tetrazolyl, pyridyl, pyrimidinyl, pyridazinyl, quinolyl, isoquinolyl, indolyl, and (in case of R^1 and R^2 being C_{7-12} aralkyl) C_{6-10} aryl and C_{7-10} aralkyl, [said group of substituents being optionally substituted with 1 to 5 same or different substituents selected from halogen, hydroxyl, C_{1-4} alkyl, C_{2-4} alkenyl, C_{2-4} alkynyl, C_{6-10} aryl, C_{1-4} alkoxy, phenoxy, C_{1-4} alkylthio, and phenylthio],

C_{2-10} alkenyl, C_{2-10} alkynyl, C_{1-4} alkoxy, C_{1-4} alkylthio, C_{1-4} alkylsulfinyl, C_{1-4} alkylsulfonyl, amino, mono- or di-C_{1-4} alkylamino, C_{3-6} cycloalkylamino, and (in case of R^1 and R^2 being C_{7-12} aralkyl) C_{1-15} alkyl, [said group of substituents being optionally substituted with 1 to 5 same or different substituents selected from halogen, hydroxyl, C_{1-4} alkoxy and C_{1-4} alkylthio],

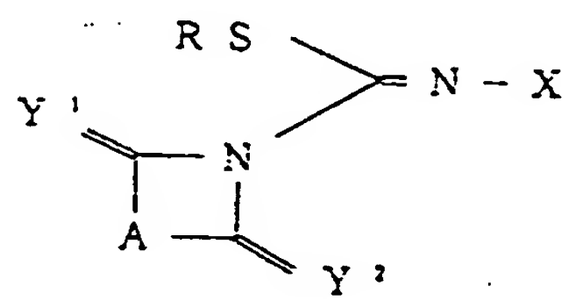
nitro, hydroxyl, mercapto, oxo, thioxo, cyano, carbamoyl, carboxyl, C_{1-4} alkoxycarbonyl, sulfo, halogen, C_{2-6} acylamino, C_{2-4} acyl, and C_{6-10} arylcarbonyl; or

R^1 and R^2 taken together with the vicinal nitrogen represent an aziridino, azetidino, pyrrolidino, morpholino, or thiomorpholino group.

8. A process for preparing a compound having the following formula, or a salt thereof:



which comprises reacting a compound of the following formula:



with a compound of the formula:

$$R^3\text{-}NH(CH_2)_n\text{-}B$$

wherein R, X, Y^1, Y^2, and A are as defined in claim 1;

n is 0 or 1;

B is C_{3-8} cycloalkyl, C_{3-8} cycloalkenyl, or C_{6-14} aryl, thienyl, furyl, pyrrolyl, pyridyl, oxazolyl, thiazolyl, pyrazolyl, imidazolyl, isoxazolyl, isothiazolyl, oxadiazolyl, thiadiazolyl, triazolyl, tetrazolyl, N-oxide-pyridyl, pyrimidinyl, N-oxide-pyrimidinyl, pyridazinyl, pyrazinyl, N-oxide-pyrazinyl, N-oxide-pyridazinyl, benzofuryl, benzothienyl, benzothiazolyl, benzoxazolyl, triazinyl, oxo-triazinyl, tetrazolo[1,5-b]pyridazinyl, triazolo[4,5-b]pyridazinyl, oxo-imidazolyl, dioxo-triazinyl, pyrrolidinyl, piperidyl, pyranyl, thiopyranyl, oxazinyl, morpholinyl, thiazinyl, piperazinyl, benzoimidazolyl, quinolyl, isoquinolyl, cinnolinyl, phthalazinyl, quinazolinyl, quinoxalinyl, indolizinyl, quinolizinyl, 1,8-naphthyridinyl, purinyl, pteridinyl, dibenzofuranyl, carbazolyl, acridinyl, phenanthridinyl, phenazinyl, phenothiazinyl, and phenoxazinyl, which may be optionally substituted with one to five same or different substituents selected from

C_{1-15} alkyl, C_{6-10} aryl, C_{7-10} aralkyl, C_{3-10} cycloalkyl, C_{2-10} alkenyl, C_{2-10} alkynyl, C_{3-10} cycloalkenyl, nitro, hydroxyl, mercapto, oxo, thioxo, cyano, carbamoyl, carboxyl, C_{1-4} alkoxycarbonyl, sulfo, halogen, C_{1-4} alkoxy, C_{6-10} aryloxy, C_{1-4} alkylthio, C_{6-10} arylthio, C_{1-4} alkylsulfinyl, C_{6-10} arylsulfinyl, C_{1-4} alkylsulfonyl, C_{6-10} arylsulfonyl, amino, C_{2-6} acylamino, mono- or di-C_{1-4} alkylamino, C_{3-6} cycloalkylamino, C_{6-10} arylamino, C_{2-4} acyl, C_{6-10} arylcarbonyl, thienyl, furyl, pyrazolyl, thiazolyl, isothiazolyl, oxazolyl, isoxazolyl, imidazolyl, triazolyl, tetrazolyl, pyridyl, pyrimidinyl, pyridazinyl, quinolyl, isoquinolyl, and indolyl; and

R^3 is hydrogen, C_{1-10} alkyl (straight, branched or cyclic), C_{2-10} alkenyl, C_{2-10} alkynyl, or C_{7-12} aralkyl, which may be optionally substituted with one to five same or different substituents selected from

C_{3-10} cycloalkyl, C_{3-10} cycloalkenyl, C_{6-10} aryloxy, C_{6-10} arylthio, C_{6-10} arylsulfinyl, C_{6-10} arylsulfonyl, C_{6-10}

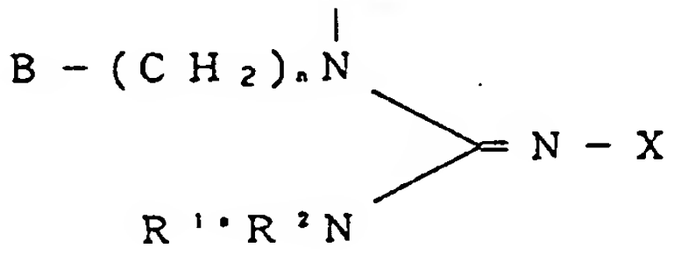
arylamino, thienyl, furyl, pyrazolyl, thiazolyl, isothiazolyl, oxazolyl, isoxazolyl, imidazolyl, triazolyl, tetrazolyl, pyridyl, pyrimidinyl, pyridazinyl, quinolyl, isoquinolyl, indolyl, and (in case of R^3 being C_{7-12} aralkyl) C_{6-10} aryl and C_{7-10} aralkyl, [said group of substituents being optionally substituted with 1 to 5 same or different substituents selected from halogen, hydroxyl, C_{1-4} alkyl, C_{2-4} alkenyl, C_{2-4} alkynyl, C_{6-10} aryl, C_{1-4} alkoxy, phenoxy, C_{1-4} alkylthio, and phenylthio],

C_{2-10} alkenyl, C_{2-10} alkynyl, C_{1-4} alkoxy, C_{1-4} alkylthio, C_{1-4} alkylsulfinyl, C_{1-4} alkylsulfonyl, amino, mono- or di-C_{1-4} alkylamino, C_{3-6} cycloalkylamino, and (in case of R^3 being C_{7-12} aralkyl) C_{1-15} alkyl, [said group of substituents being optionally substituted with 1 to 5 same or different substituents selected from

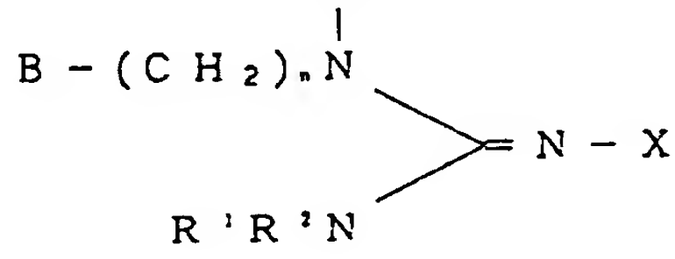
halogen, hydroxyl, C_{1-4} alkoxy and C_{1-4} alkylthio],

nitro, hydroxyl, mercapto, oxo, thioxo, cyano, carbamoyl, carboxyl, C_{1-4} alkoxycarbonyl, sulfo, halogen, C_{2-6} acylamino, C_{2-4} acyl, and C_{6-10} arylcarbonyl.

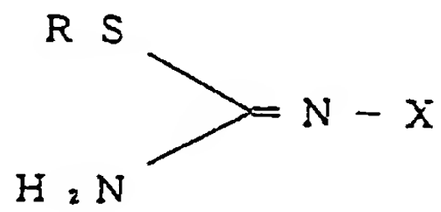
9. A process for preparing a compound having the following formula, or a salt thereof:



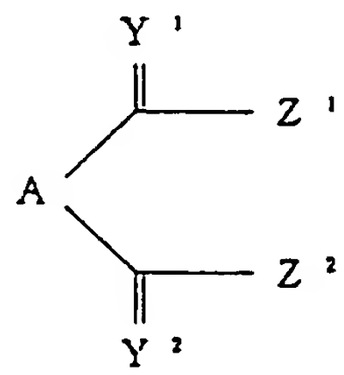
or



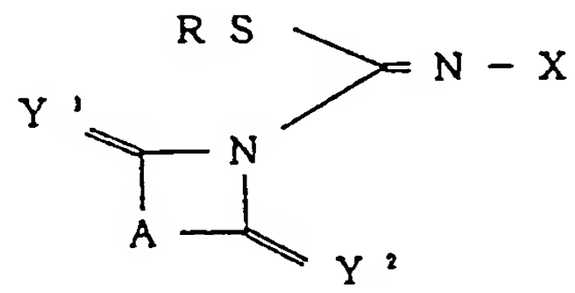
which comprises reacting a compound of the following formula:



with a compound of the following formula:



and then reacting the compound produced having the following formula



i) with an amine having the formula:

R^1R^2NH

or a salt thereof followed by reaction of a compound of the formula:

R^3-$NH(CH_2)_n$-B

after acylation if necessary when R^1 represents a hydrogen atom; or
ii) with a compound of the formula:

R^3-$NH(CH_2)_n$-B

followed by reaction of an amine having the formula

R^1R^2NH

or a salt thereof, after acylation if necessary when R^3 represents a hydrogen atom,
wherein A, R, X, Y^1 and Y^2 are of the same meaning as defined in claim 1;
B, n, R^1, R^2,R^3, Z^1 and Z^2 are of the same meaning as defined in claims 6, 7 and 8;

R^{1a} is of the same meaning as R^1, and additionally can be C_{1-10} acyl (aliphatic, alicyclic, aromatic, or heterocyclic), which may be optionally substituted with one to five same or different substituents selected from

C_{3-10} cycloalkyl, C_{3-10} cycloalkenyl, C_{6-10} aryloxy, C_{6-10} arylthio, C_{6-10} arylsulfinyl, C_{6-10} arylsulfonyl, C_{6-10} arylamino, C_{6-10} aryl, C_{7-10} aralkyl, thienyl, furyl, pyrazolyl, thiazolyl, isothiazolyl, oxazolyl, isoxazolyl, imidazolyl, triazolyl, tetrazolyl, pyridyl, pyrimidinyl, pyridazinyl, quinolyl, isoquinolyl, and indolyl, [said group of substituents being optionally substituted with 1 to 5 same or different substituents selected from halogen, hydroxyl, C_{1-4} alkyl, C_{2-4} alkenyl, C_{2-4} alkynyl, C_{6-10} aryl, C_{1-4} alkoxy, phenoxy, C_{1-4} alkylthio, and phenylthio],

C_{2-10} alkenyl, C_{2-10} alkynyl, C_{1-4} alkoxy, C_{1-4} alkylthio, C_{1-4} alkylsulfinyl, C_{1-4} alkylsulfonyl, amino, mono- or di-C_{1-4} alkylamino, C_{3-6} cycloalkylamino, C_{1-15} alkyl, [said group of substituents being optionally substituted with 1 to 5 same or different substituents selected from

halogen, hydroxyl, C_{1-4} alkoxy and C_{1-4} alkylthio],

nitro, hydroxyl, mercapto, oxo, thioxo, cyano, carbamoyl, carboxyl, C_{1-4} alkoxycarbonyl, sulfo, halogen, C_{2-6} acylamino, C_{2-4} acyl, and C_{6-10} arylcarbonyl; or
R^{1a} and R^2 taken together with the vicinal nitrogen represent a cyclic amino group; and
R^{3a} is of the same meaning as R^3, and additionally can be C_{1-10} acyl (aliphatic, alicyclic, aromatic, or heterocyclic), which may be optionally substituted with one to five same or different substituent groups selected from

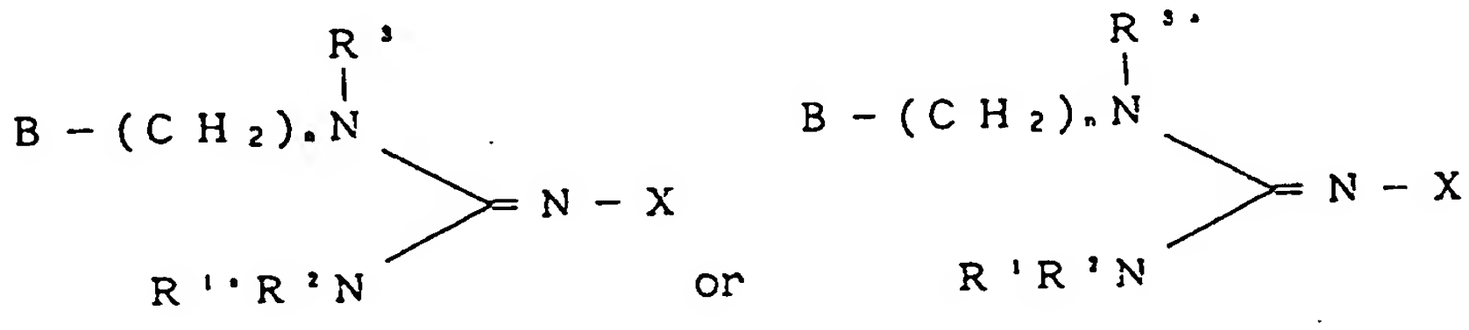
C_{3-10} cycloalkyl, C_{3-10} cycloalkenyl, C_{6-10} aryloxy, C_{6-10} arylthio, C_{6-10} arylsulfinyl, C_{6-10} arylsulfonyl, C_{6-10} arylamino, C_{6-10} aryl, C_{7-10} aralkyl, thienyl, furyl, pyrazolyl, thiazolyl, isothiazolyl, oxazolyl, isoxazolyl, imidazolyl, triazolyl, tetrazolyl, pyridyl, pyrimidinyl, pyridazinyl, quinolyl, isoquinolyl, and indolyl, [said group of substituents being optionally substituted with 1 to 5 same or different substituents selected from halogen, hydroxyl, C_{1-4} alkyl, C_{2-4} alkenyl, C_{2-4} alkynyl, C_{6-10} aryl, C_{1-4} alkoxy, phenoxy, C_{1-4} alkylthio, and phenylthio],

C_{2-10} alkenyl, C_{2-10} alkynyl, C_{1-4} alkoxy, C_{1-4} alkylthio, C_{1-4} alkylsulfinyl, C_{1-4} alkylsulfonyl, amino, mono- or di-C_{1-4} alkylamino, C_{3-6} cycloalkylamino, C_{1-15} alkyl, [said group of substituents being optionally substituted with 1 to 5 same or different substituents selected from

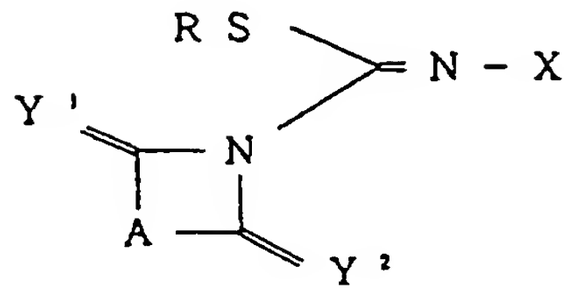
halogen, hydroxyl, C_{1-4} alkoxy and C_{1-4} alkylthio],

nitro, hydroxyl, mercapto, oxo, thioxo, cyano, carbamoyl, carboxyl, C_{1-4} alkoxycarbonyl, sulfo, halogen, C_{2-6} acylamino, C_{2-4} acyl, and C_{6-10} arylcarbonyl.

10. A process for preparing a copound having the following formula, or a salt thereof:



which comprises reacting a compound of the following formula:



i) with an amine having the formula:

$$R^1R^2NH$$

or a salt thereof followed by reaction of a compound of the formula:

$$R^3\text{-}NH(CH_2)_n\text{-}B$$

after acylation if necessary when R^1 represents a hydrogen atom; or
ii) with a compound of the formula:

$$R^3\text{-}NH(CH_2)_n\text{-}B$$

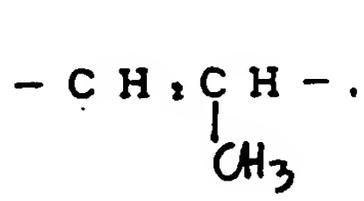
followed by reaction of an amine having the formula

$$R^1R^2NH$$

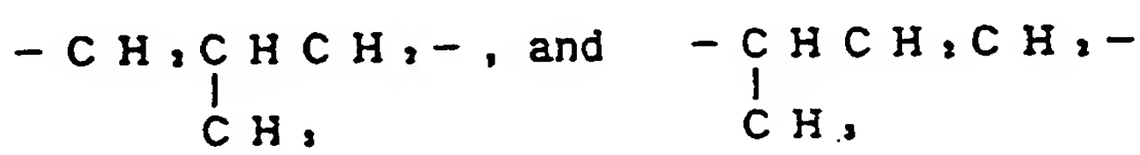
or a salt thereof, after acylation if necessary when R^3 represents a hydrogen atom,
wherein A, R, X, Y^1 and Y^2 are of the same meaning as defined in claim 1;
B, n, R^1, R^2 and R^3 are of the same meaning as defined in claims 7 and 8; and
R^{1a} and R^{3a} are of the same meaning as defined in claim 9.

11. A process according to any one of claims 6-10 wherein R is $C_{1\text{-}10}$ alkyl, or $C_{7\text{-}12}$ aralkyl.

12. A process according to any one of claims 6-10 wherein A is $C_{1\text{-}4}$ alkylene selected from
$-CH_2-$, $-CH_2CH_2-$, $-CH_2CH_2CH_2-$,



$-(CH_2)_4-$,



13. A process according to any one of claims 6-10, wherein A is o-phenylene, 1,2-ethylene or 1,3-propylene.

14. A process according to any one of claims 6-10, wherein said electron withdrawing group X is cyano, or nitro.

15. A process according to claim 7 or 10, wherein said R^1R^2N group is an unsubstituted amino, mono-$C_{1\text{-}4}$ alkylamino,

or di-C_{1-4} alkylamino group.

16. A process according to claim 9 or 10, wherein R^{1a} is C_{1-10} alkyl, C_{7-12} aralkyl, C_{1-4} acyl.

17. A process according to claim 9 or 10, wherein said $R^{1a}R^2N$ group is an unsubstituted amino, mono-C_{1-4} alkylamino, di-C_{1-4} alkylamino, C_{1-4} acylamino, or N-C_{1-2} acyl-N-C_{1-4} alkylamino group.

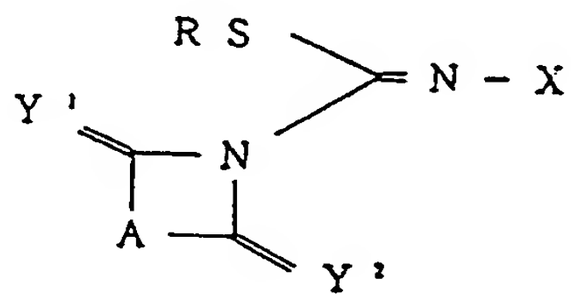
18. A process according to any one of claims 8-10, wherein B is pyridyl and thiazolyl which may be substituted with one or two halogens.

19. A process according to claim 9 or 10, wherein R^{3a} is C_{1-10} alkyl, or C_{7-12} aralkyl.

20. A process according to any one of claims 7, 9 or 10, wherein said R^1R^2N group is an unsubstituted amino, mono-C_{1-4} alkylamino, di-C_{1-4} alkylamino group aziridino, azetidino, pyrrolidino, morpholino, or thiomorpholino.

Claims for the following Contracting State : ES

1. A process for preparing a compound having the following formula:



wherein

R is C_{1-10} alkyl (straight, branched or cyclic), C_{2-10} alkenyl, C_{2-10} alkynyl, C_{7-12} aralkyl, or C_{1-10} acyl (aliphatic, alicyclic, aromatic, or heterocyclic), which may be optionally substituted with one to five same or different substituents selected from

C_{3-10} cycloalkyl, C_{3-10} cycloalkenyl, C_{6-10} aryloxy, C_{6-10} arylthio, C_{6-10} arylsulfinyl, C_{6-10} arylsulfonyl, C_{6-10} arylamino, thienyl, furyl, pyrazolyl, thiazolyl, isothiazolyl, oxazolyl, isoxazolyl, imidazolyl, triazolyl, tetrazolyl, pyridyl, pyrimidinyl, pyridazinyl, quinolyl, isoquinolyl, indolyl, and (in case of R being C_{7-12} aralkyl and C_{1-10} acyl) C_{6-10} aryl and C_{7-10} aralkyl,

C_{2-10} alkenyl, C_{2-10} alkynyl, C_{1-4} alkoxy, C_{1-4} alkylthio, C_{1-4} alkylsulfinyl, C_{1-4} alkylsulfonyl, amino, mono- or di-C_{1-4} alkylamino, C_{3-6} cycloalkylamino, and (in case of R being C_{7-12} aralkyl and C_{1-10} acyl) C_{1-15} alkyl,

nitro, hydroxyl, mercapto, oxo, thioxo, cyano, carbamoyl, carboxyl, C_{1-4} alkoxycarbonyl, sulfo, halogen, C_{2-6} acylamino, C_{2-4} acyl, and C_{6-10} arylcarbonyl;

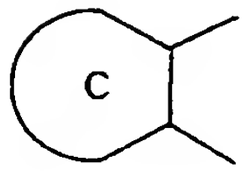
X is an electron withdrawing group selected from cyano, nitro, alkoxycarbonyl, hydroxycarbonyl, C_{6-10} aryloxycarbonyl, C_{1-4} alkylsulfonyl (optionally substituted with halogen), sulfamoyl, di-C_{1-4} alkoxyphosphoryl, C_{1-4} acyl (optionally substituted with halogen), carbamoyl, C_{1-4} alkylsulfonylthiocarbamoyl, thienyloxycarbonyl, furyloxycarbonyl, pyrazolyloxycarbonyl, thiazolyloxycarbonyl, isothiazolyloxycarbonyl, oxazolyloxycarbonyl, isoxazolyloxycarbonyl, imidazolyloxycarbonyl, triazolyloxycarbonyl, tetrazolyloxycarbonyl, pyridyloxycarbonyl, pyrimidinyloxycarbonyl, pyridazinyloxycarbonyl, quinolyloxycarbonyl, isoquinolyloxycarbonyl, and indolyloxycarbonyl;

Y^1 and Y^2, which are the same or different, are each independently oxygen or sulfur; and

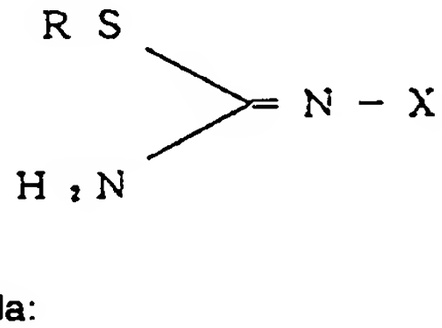
A is a divalent hydrocarbon residue selected from C_{1-4} alkylene,

and a cyclic group

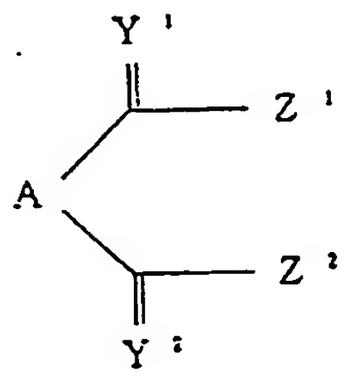
represented by the following formula:



wherein the C-ring represents benzene or cyclohexane, which process comprises reacting a compound of the following formula:



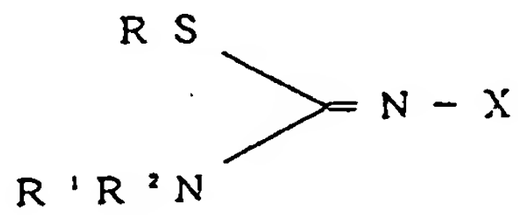
with a compound of the following formula:



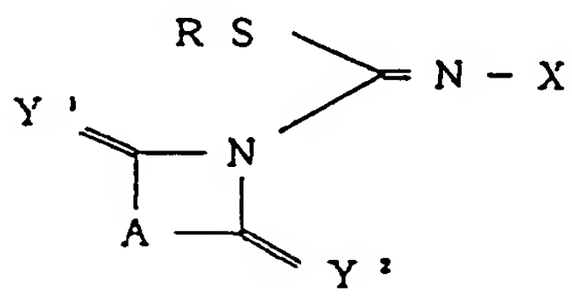
wherein

A, R, X, Y^1 and Y^2 are of the same meaning as defined above; and
Z^1 and Z^2, which are the same or different, are selected from fluorine, chlorine and bromine; or
Z^1 and Z^2 taken together represent oxygen.

2. A process for preparing a compound having the following formula, or a salt thereof:



which comprises reacting a compound of the following formula:



with a compound of the following formula:

R^1R^2NH

wherein

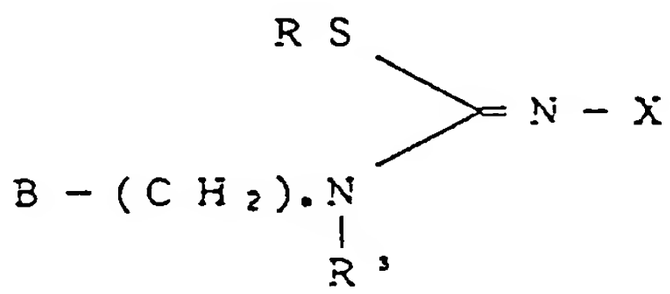
A, R, X, Y^1 and Y^2 are of the same meaning as defined in claim 1; and
R^1 and R^2, which are the same or different, are each independently hydrogen, C_{1-10} alkyl (straight, branched, or cyclic), C_{2-10} alkenyl, C_{2-10} alkynyl, or C_{7-12} aralkyl, which may be optionally substituted with one to five same or different substituents selected from

C_{3-10} cycloalkyl, C_{3-10} cycloalkenyl, C_{6-10} aryloxy, C_{6-10} arylthio, C_{6-10} arylsulfinyl, C_{6-10} arylsulfonyl, C_{6-10} arylamino, thienyl, furyl, pyrazolyl, thiazolyl, isothiazolyl, oxazolyl, isoxazolyl, imidazolyl, triazolyl, tetrazolyl, pyridyl, pyrimidinyl, pyridazinyl, quinolyl, isoquinolyl, indolyl, and (in case of R^1 and R^2 being C_{7-12} aralkyl) C_{6-10} aryl and C_{7-10} aralkyl, [said group of substituents being optionally substituted with 1 to 5 same or different substituents selected from halogen, hydroxyl, C_{1-4} alkyl, C_{2-4} alkenyl, C_{2-4} alkynyl, C_{6-10} aryl, C_{1-4} alkoxy, phenoxy, C_{1-4} alkylthio, and phenylthio],

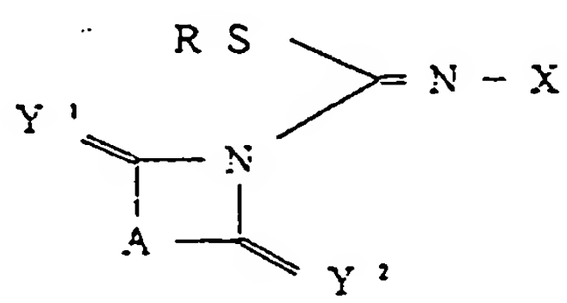
C_{2-10} alkenyl, C_{2-10} alkynyl, C_{1-4} alkoxy, C_{1-4} alkylthio, C_{1-4} alkylsulfinyl, C_{1-4} alkylsulfonyl, amino, mono- or di-C_{1-4} alkylamino, C_{3-6} cycloalkylamino, and (in case of R^1 and R^2 being C_{7-12} aralkyl) C_{1-15} alkyl, [said group of substituents being optionally substituted with 1 to 5 same or different substituents selected from halogen, hydroxyl, C_{1-4} alkoxy and C_{1-4} alkylthio],

nitro, hydroxyl, mercapto, oxo, thioxo, cyano, carbamoyl, carboxyl, C_{1-4} alkoxycarbonyl, sulfo, halogen, C_{2-6} acylamino, C_{2-4} acyl, and C_{6-10} arylcarbonyl; or
R^1 and R^2 taken together with the vicinal nitrogen represent an aziridino, azetidino, pyrrolidino, morpholino, or thiomorpholino group.

3. A process for preparing a compound having the following formula, or a salt thereof:



which comprises reacting a compound of the following formula:



with a compound of the formula:

$$R^3\text{-}NH(CH_2)_n\text{-}B$$

wherein R, X, Y^1, Y^2, and A are as defined in claim 1;
n is 0 or 1;
B is C_{3-8} cycloalkyl, C_{3-8} cycloalkenyl, or C_{6-14} aryl, thienyl, furyl, pyrrolyl, pyridyl, oxazolyl, thiazolyl, pyrazolyl, imidazolyl, isoxazolyl, isothiazolyl, oxadiazolyl, thiadiazolyl, triazolyl, tetrazolyl, N-oxide-pyridyl, pyrimidinyl, N-oxide-pyrimidinyl, pyridazinyl, pyrazinyl, N-oxide-pyrazinyl, N-oxide-pyridazinyl, benzofuryl, benzothienyl, benzothiazolyl, benzoxazolyl, triazinyl, oxo-triazinyl, tetrazolo[1,5-b]pyridazinyl, triazolo[4,5-b]pyridazinyl, oxo-imidazolyl, dioxo-triazinyl, pyrrolidinyl, piperidyl, pyranyl, thiopyranyl, oxazinyl, morpholinyl, thiazinyl, piperazinyl, benzoimidazolyl, quinolyl, isoquinolyl, cinnolinyl, phthalazinyl, quinazolinyl, quinoxalinyl, indolizinyl, quinolizinyl, 1,8-naphthyridinyl, purinyl, pteridinyl, dibenzofuranyl, carbazolyl, acridinyl, phenanthridinyl, phenazinyl, phenothiazinyl, and phenoxazinyl, which may be optionally substituted with one to five same or different substituents selected from

C_{1-15} alkyl, C_{6-10} aryl, C_{7-10} aralkyl, C_{3-10} cycloalkyl, C_{2-10} alkenyl, C_{2-10} alkynyl, C_{3-10} cycloalkenyl, nitro,

hydroxyl, mercapto, oxo, thioxo, cyano, carbamoyl, carboxyl, C_{1-4} alkoxycarbonyl, sulfo, halogen, C_{1-4} alkoxy, C_{6-10} aryloxy, C_{1-4} alkylthio, C_{6-10} arylthio, C_{1-4} alkylsulfinyl, C_{6-10} arylsulfinyl, C_{1-4} alkylsulfonyl, C_{6-10} arylsulfonyl, amino, C_{2-6} acylamino, mono- or di-C_{1-4} alkylamino, C_{3-6} cycloalkylamino, C_{6-10} arylamino, C_{2-4} acyl, C_{6-10} arylcarbonyl, thienyl, furyl, pyrazolyl, thiazolyl, isothiazolyl, oxazolyl, isoxazolyl, imidazolyl, triazolyl, tetrazolyl, pyridyl, pyrimidinyl, pyridazinyl, quinolyl, isoquinolyl, and indolyl; and

R^3 is hydrogen, C_{1-10} alkyl (straight, branched or cyclic), C_{2-10} alkenyl, C_{2-10} alkynyl, or C_{7-12} aralkyl, which may be optionally substituted with one to five same or different substituents selected from

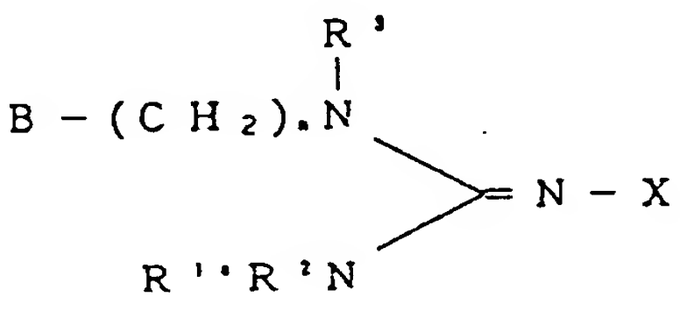
C_{3-10} cycloalkyl, C_{3-10} cycloalkenyl, C_{6-10} aryloxy, C_{6-10} arylthio, C_{6-10} arylsulfinyl, C_{6-10} arylsulfonyl, C_{6-10} arylamino, thienyl, furyl, pyrazolyl, thiazolyl, isothiazolyl, oxazolyl, isoxazolyl, imidazolyl, triazolyl, tetrazolyl, pyridyl, pyrimidinyl, pyridazinyl, quinolyl, isoquinolyl, indolyl, and (in case of R^3 being C_{7-12} aralkyl) C_{6-10} aryl and C_{7-10} aralkyl, [said group of substituents being optionally substituted with 1 to 5 same or different substituents selected from halogen, hydroxyl, C_{1-4} alkyl, C_{2-4} alkenyl, C_{2-4} alkynyl, C_{6-10} aryl, C_{1-4} alkoxy, phenoxy, C_{1-4} alkylthio, and phenylthio],

C_{2-10} alkenyl, C_{2-10} alkynyl, C_{1-4} alkoxy, C_{1-4} alkylthio, C_{1-4} alkylsulfinyl, C_{1-4} alkylsulfonyl, amino, mono- or di-C_{1-4} alkylamino, C_{3-6} cycloalkylamino, and (in case of R^3 being C_{7-12} aralkyl) C_{1-15} alkyl, [said group of substituents being optionally substituted with 1 to 5 same or different substituents selected from

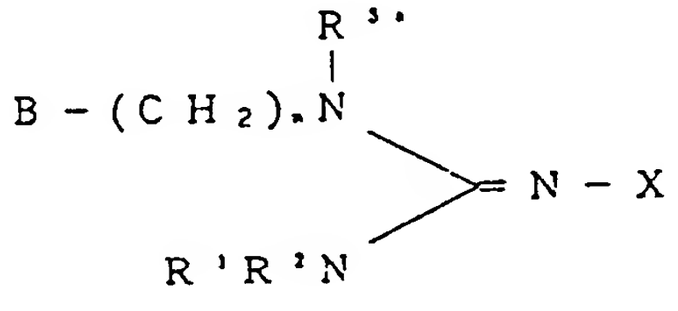
halogen, hydroxyl, C_{1-4} alkoxy and C_{1-4} alkylthio],

nitro, hydroxyl, mercapto, oxo, thioxo, cyano, carbamoyl, carboxyl, C_{1-4} alkoxycarbonyl, sulfo, halogen, C_{2-6} acylamino, C_{2-4} acyl, and C_{6-10} arylcarbonyl.

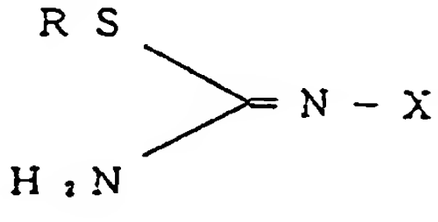
4. A process for preparing a compound having the following formula, or a salt thereof:



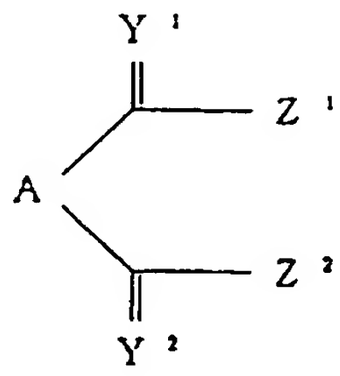
or



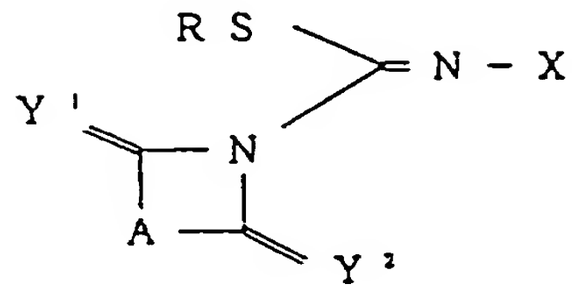
which comprises reacting a compound of the following formula:



with a compound of the following formula:



and then reacting the compound produced having the following formula



i) with an amine having the formula:

$$R^1R^2NH$$

or a salt thereof followed by reaction of a compound of the formula:

$$R^3\text{-}NH(CH_2)_n\text{-}B$$

after acylation if necessary when R^1 represents a hydrogen atom; or
ii) with a compound of the formula:

$$R^3\text{-}NH(CH_2)_n\text{-}B$$

followed by reaction of an amine having the formula

$$R^1R^2NH$$

or a salt thereof, after acylation if necessary when R^3 represents a hydrogen atom,
wherein A, R, X, Y^1, Y^2, Z^1 and Z^2 are of the same meaning as defined in claim 1;
B, n, R^1, R^2 and R^3 are of the same meaning as defined in claims 2 and 3;

R^{1a} is of the same meaning as R^1, and additionally can be $C_{1\text{-}10}$ acyl (aliphatic, alicyclic, aromatic, or heterocyclic), which may be optionally substituted with one to five same or different substituents selected from

$C_{3\text{-}10}$ cycloalkyl, $C_{3\text{-}10}$ cycloalkenyl, $C_{6\text{-}10}$ aryloxy, $C_{6\text{-}10}$ arylthio, $C_{6\text{-}10}$ arylsulfinyl, $C_{6\text{-}10}$ arylsulfonyl, $C_{6\text{-}10}$ arylamino, $C_{6\text{-}10}$ aryl, $C_{7\text{-}10}$ aralkyl, thienyl, furyl, pyrazolyl, thiazolyl, isothiazolyl, oxazolyl, isoxazolyl, imidazolyl, triazolyl, tetrazolyl, pyridyl, pyrimidinyl, pyridazinyl, quinolyl, isoquinolyl, and indolyl, [said group of substituents being optionally substituted with 1 to 5 same or different substituents selected from halogen, hydroxyl, $C_{1\text{-}4}$ alkyl, $C_{2\text{-}4}$ alkenyl, $C_{2\text{-}4}$ alkynyl, $C_{6\text{-}10}$ aryl, $C_{1\text{-}4}$ alkoxy, phenoxy, $C_{1\text{-}4}$ alkylthio, and phenylthio],

$C_{2\text{-}10}$ alkenyl, $C_{2\text{-}10}$ alkynyl, $C_{1\text{-}4}$ alkoxy, $C_{1\text{-}4}$ alkylthio, $C_{1\text{-}4}$ alkylsulfinyl, $C_{1\text{-}4}$ alkylsulfonyl, amino, mono- or di-$C_{1\text{-}4}$ alkylamino, $C_{3\text{-}6}$ cycloalkylamino, $C_{1\text{-}15}$ alkyl, [said group of substituents being optionally substituted with 1 to 5 same or different substituents selected from

halogen, hydroxyl, $C_{1\text{-}4}$ alkoxy and $C_{1\text{-}4}$ alkylthio],

nitro, hydroxyl, mercapto, oxo, thioxo, cyano, carbamoyl, carboxyl, $C_{1\text{-}4}$ alkoxycarbonyl, sulfo, halogen, $C_{2\text{-}6}$ acylamino, $C_{2\text{-}4}$ acyl, and $C_{6\text{-}10}$ arylcarbonyl; or
R^{1a} and R^2 taken together with the vicinal nitrogen represent a cyclic amino group; and
R^{3a} is of the same meaning as R^3, and additionally can be $C_{1\text{-}10}$ acyl (aliphatic, alicyclic, aromatic, or heterocyclic), which may be optionally substituted with one to five same or different substituent groups selected from

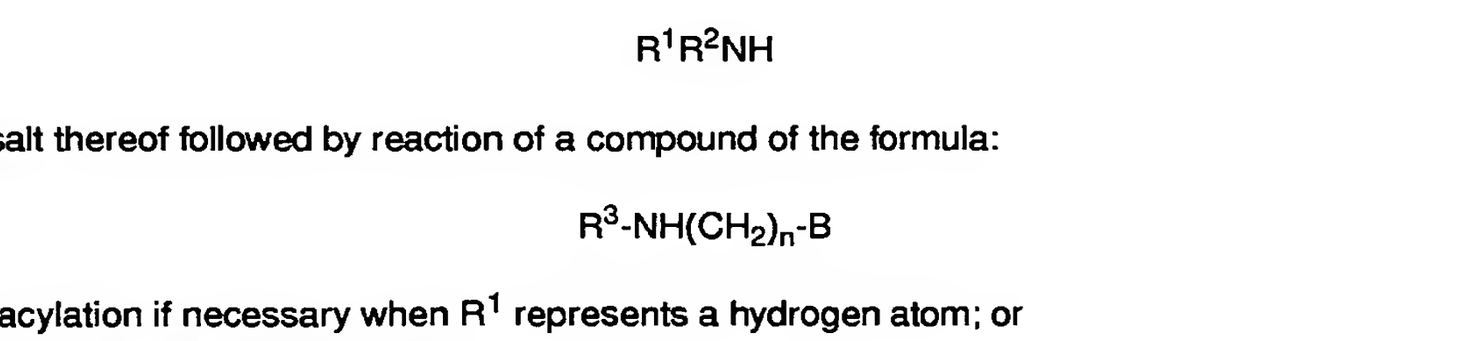
$C_{3\text{-}10}$ cycloalkyl, $C_{3\text{-}10}$ cycloalkenyl, $C_{6\text{-}10}$ aryloxy, $C_{6\text{-}10}$ arylthio, $C_{6\text{-}10}$ arylsulfinyl, $C_{6\text{-}10}$ arylsulfonyl, $C_{6\text{-}10}$ arylamino, $C_{6\text{-}10}$ aryl, $C_{7\text{-}10}$ aralkyl, thienyl, furyl, pyrazolyl, thiazolyl, isothiazolyl, oxazolyl, isoxazolyl, imidazolyl, triazolyl, tetrazolyl, pyridyl, pyrimidinyl, pyridazinyl, quinolyl, isoquinolyl, and indolyl, [said group of substituents being optionally substituted with 1 to 5 same or different substituents selected from halogen, hydroxyl, $C_{1\text{-}4}$ alkyl, $C_{2\text{-}4}$ alkenyl, $C_{2\text{-}4}$ alkynyl, $C_{6\text{-}10}$ aryl, $C_{1\text{-}4}$ alkoxy, phenoxy, $C_{1\text{-}4}$ alkylthio, and phenylthio],

$C_{2\text{-}10}$ alkenyl, $C_{2\text{-}10}$ alkynyl, $C_{1\text{-}4}$ alkoxy, $C_{1\text{-}4}$ alkylthio, $C_{1\text{-}4}$ alkylsulfinyl, $C_{1\text{-}4}$ alkylsulfonyl, amino, mono- or di-$C_{1\text{-}4}$ alkylamino, $C_{3\text{-}6}$ cycloalkylamino, $C_{1\text{-}15}$ alkyl, [said group of substituents being optionally substituted with 1 to 5 same or different substituents selected from

halogen, hydroxyl, $C_{1\text{-}4}$ alkoxy and $C_{1\text{-}4}$ alkylthio],

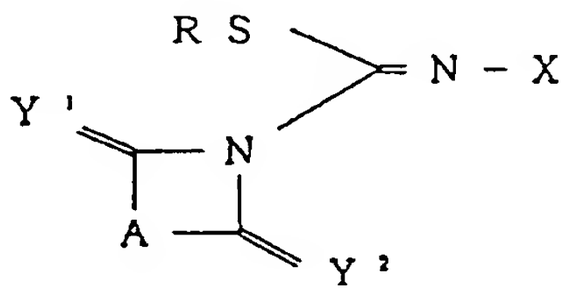
nitro, hydroxyl, mercapto, oxo, thioxo, cyano, carbamoyl, carboxyl, C_{1-4} alkoxycarbonyl, sulfo, halogen, C_{2-6} acylamino, C_{2-4} acyl, and C_{6-10} arylcarbonyl.

5. A process for preparing a copound having the following formula, or a salt thereof:



or

which comprises reacting a compound of the following formula:



i) with an amine having the formula:

$$R^1R^2NH$$

or a salt thereof followed by reaction of a compound of the formula:

$$R^3\text{-}NH(CH_2)_n\text{-}B$$

after acylation if necessary when R^1 represents a hydrogen atom; or
ii) with a compound of the formula:

$$R^3\text{-}NH(CH_2)_n\text{-}B$$

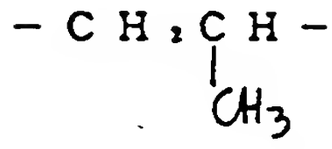
followed by reaction of an amine having the formula

$$R^1R^2NH$$

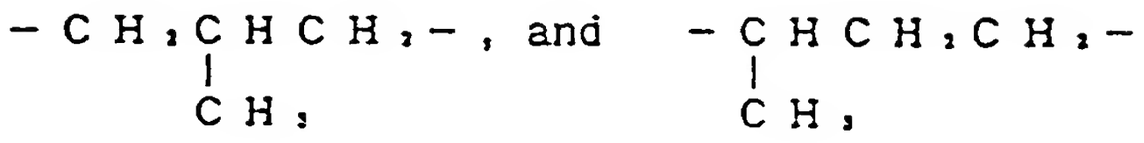
or a salt thereof, after acylation if necessary when R^3 represents a hydrogen atom,
wherein A, R, X, Y^1 and Y^2 are of the same meaning as defined in claim 1;
B, n, R^1, R^2 and R^3 are of the same meaning as defined in claims 2 and 3; and
R^{1a} and R^{3a} are of the same meaning as defined in claim

6. The process according to any one of claims 1-5, wherein R is C_{1-10} alkyl, or C_{7-12} aralkyl.

7. The process according to any one of claims 1-5, wherein A is C_{1-4} alkylene selected from
$-CH_2-$, $-CH_2CH_2-$, $-CH_2CH_2CH_2-$,



-$(CH_2)_4$-,



8. The process according to any one of claims 1-5, wherein A is o-phenylene, 1,2-ethylene or 1,3-propylene.

9. The process according to any one of claims 1-5, wherein said electron withdrawing group X is cyano, or nitro.

10. The process according to claim 2 or 5 wherein said R^1R^2N group is an unsubstituted amino, mono-C_{1-4} alkylamino, or di-C_{1-4} alkylamino group.

11. The process according to claim 4 or 5, wherein R^{1a} is C_{1-10} alkyl, C_{7-12} aralkyl, C_{1-4} acyl.

12. The process according to claim 4 or 5, wherein said $R^{1a}R^2N$ group is an unsubstituted amino, mono-C_{1-4} alkylamino, di-C_{1-4} alkylamino, C_{1-4} acylamino, or N-C_{1-2} acyl-N-C_{1-4} alkylamino group.

13. The process according to any one of claims 3-5, wherein B is pyridyl and thiazolyl which may be substituted with one or two halogens.

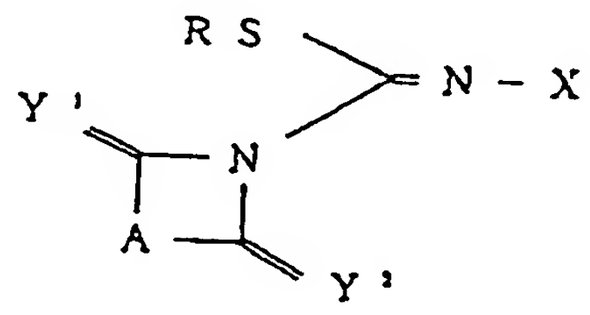
14. The process according to claim 4 or 5, wherein R^{3a} is C_{1-10} alkyl, or C_{7-12} aralkyl.

15. The process according to any one of claims 2, 4 or 5, wherein said R^1R^2N group is an unsubstituted amino, mono-C_{1-4} alkylamino, di-C_{1-4} alkylamino group aziridino, azetidino, pyrrolidino, morpholino, or thiomorpholino.

Patentansprüche

Patentansprüche für folgende Vertragsstaaten : AT, BE, CH, DE, DK, FR, GB, GR, IT, LI, LU, NL, SE

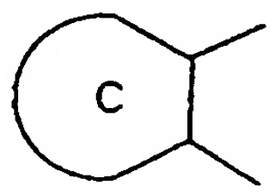
1. Verbindung mit der folgenden Formel:



wobei

R C_{1-10}-Alkyl (geradkettig, verzweigt oder cyclisch), C_{2-10}-Alkenyl, C_{2-10}-Alkinyl, C_{7-12}-Aralkyl oder C_{1-10}-Acyl (aliphatisch, alicyclisch, aromatisch oder heterocyclisch) ist, das gegebenenfalls mit einem bis fünf gleichen oder verschiedenen Substituenten substituiert sein kann, die ausgewählt sind aus C_{3-10}-Cycloalkyl, C_{3-10}-Cycloalkenyl, C_{6-10}-Aryloxy, C_{6-10}-Arylthio, C_{6-10}-Arylsulfinyl, C_{6-10}-Arylsulfonyl, C_{6-10}-Arylamino, Thienyl, Furyl, Pyrazolyl, Thiazolyl, Isothiazolyl, Oxazolyl, Isoxazolyl, Imidazolyl, Triazolyl, Tetrazolyl, Pyridyl, Pyrimidinyl, Pyridazinyl, Chinolyl, Isochinolyl, Indolyl sowie (im Falle, daß R C_{7-12}-Aralkyl oder C_{1-}

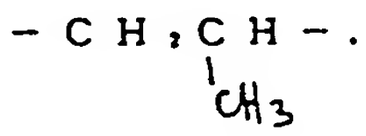
$_{10}$-Acyl ist) C_{6-10}-Aryl und C_{7-10}-Aralkyl;
C_{2-10}-Alkenyl, C_{2-10}-Alkinyl, C_{1-4}-Alkoxy, C_{1-4}-Alkylthio, C_{1-4}-Alkylsulfinyl, C_{1-4}-Alkylsulfonyl, Amino, Mono- oder Di-C_{1-4}-Alkylamino, C_{3-6}-Cycloalkylamino sowie (im Falle, daß R C_{7-12}-Aralkyl oder C_{1-10}-Acyl ist) C_{1-15}-Alkyl;
Nitro, Hydroxy, Mercapto, Oxo, Thioxo, Cyano, Carbamoyl, Carboxy, C_{1-4}-Alkoxycarbonyl, Sulfo, Halogen, C_{2-6}-Acylamino, C_{2-4}-Acyl und C_{6-10}-Arylcarbonyl;
X eine elektronenziehende Gruppe ist, die ausgewählt ist aus Cyano, Nitro, Alkoxycarbonyl, Hydroxycarbonyl, C_{6-10}-Aryloxycarbonyl, C_{1-4}-Alkylsulfonyl (gegebenenfalls mit Halogen substituiert), Sulfamoyl, Di-C_{1-4}-Alkoxyphosphoryl, C_{1-4}-Acyl (gegebenenfalls mit Halogen substituiert), Carbamoyl, C_{1-4}-Alkylsulfonylthiocarbamoyl, Thienyloxycarbonyl, Furyloxycarbonyl, Pyrazolyloxycarbonyl, Thiazolyloxycarbonyl, Isothiazolyloxycarbonyl, Oxazolyloxycarbonyl, Isoxazolyloxycarbonyl, Imidazolyloxycarbonyl, Triazolyloxycarbonyl, Tetrazolyloxycarbonyl, Pyridyloxycarbonyl, Pyrimidinyloxycarbonyl, Pyridazinyloxycarbonyl, Chinolyloxycarbonyl, Isochinolyloxycarbonyl und Indolyloxycarbonyl;
Y^1 und Y^2, die gleich oder verschieden sind, jeweils unabhängig Sauerstoff oder Schwefel sind; und
A ein Zweiwertiger Kohlenwasserstoffrest ist, der ausgewählt ist aus C_{1-4}-Alkylen und einer cyclischen Gruppe, die durch die folgende Formel dargestellt wird:



wobei der C-Ring Benzol oder Cyclohexan darstellt.

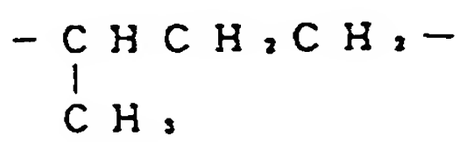
2. Verbindung gemäß Anspruch 1, wobei R C_{1-10}-Alkyl oder C_{7-12}-Aralkyl ist.

3. Verbindung gemäß Anspruch 1, wobei A ein C_{1-4}-Alkylen ist, das ausgewählt ist aus
$-CH_2-$, $-CH_2CH_2-$, $-CH_2CH_2CH_2-$,



$-(CH_2)_4-$,

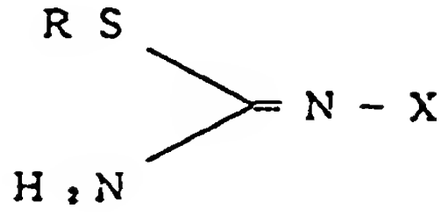
und



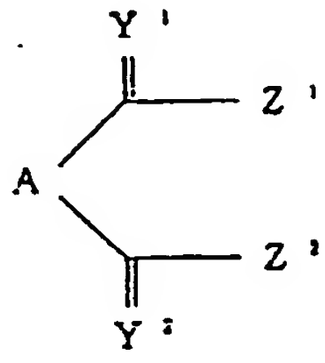
4. Verbindung gemäß Anspruch 1, wobei A o-Phenylen, 1,2-Ethylen oder 1,3-Propylen ist.

5. Verbindung gemäß Anspruch 1, wobei es sich bei der elektronenziehenden Gruppe X um Cyano oder Nitro handelt.

6. Verfahren zur Herstellung der Verbindung gemäß Anspruch 1, umfassend das Umsetzen einer Verbindung der folgenden Formel:

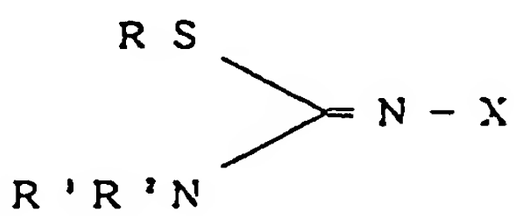


mit einer Verbindung der folgenden Formel:

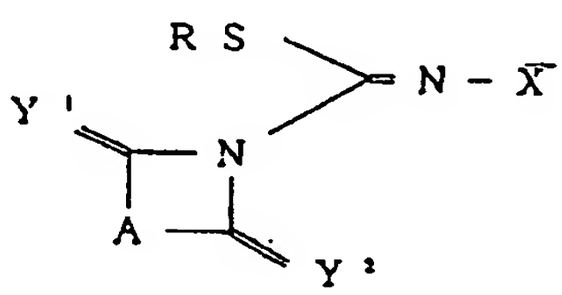


wobei A, R, X, Y^1 und Y^2 dasselbe wie in Anspruch 1 bedeuten und Z^1 und Z^2, die gleich oder verschieden sind, aus Fluor, Chlor und Brom ausgewählt sind oder Z^1 und Z^2 zusammengenommen Sauerstoff darstellen.

7. Verfahren zur Herstellung einer Verbindung der folgenden Formel oder eines Salzes davon:



umfassend das Umsetzen einer Verbindung der folgenden Formel:



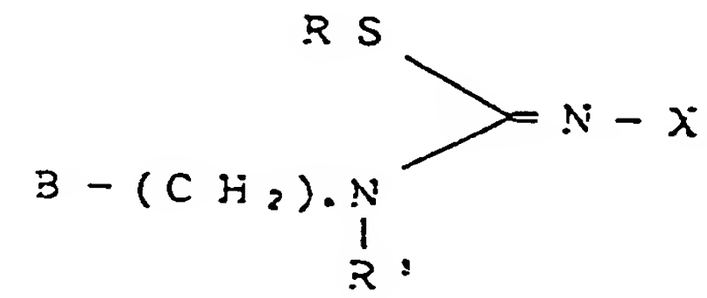
mit einer Verbindung der folgenden Formel:

$$R^1R^2NH,$$

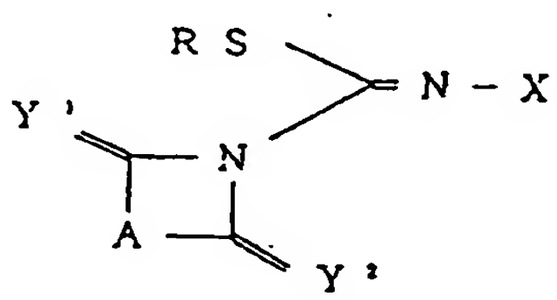
wobei A, R, X, Y^1 und Y^2 dasselbe wie in Anspruch 1 bedeuten und R^1 und R^2, die gleich oder verschieden sind, jeweils unabhängig Wasserstoff, C_{1-10}-Alkyl (geradkettig, verzweigt oder cyclisch), C_{2-10}-Alkenyl, C_{2-10}-Alkinyl oder C_{7-12}-Aralkyl sind, die gegebenenfalls mit einem bis fünf gleichen oder verschiedenen Substituenten substituiert sein können, die ausgewählt sind aus
C_{3-10}-Cycloalkyl, C_{3-10}-Cycloalkenyl, C_{6-10}-Aryloxy, C_{6-10}-Arylthio, C_{6-10}-Arylsulfinyl, C_{6-10}-Arylsulfonyl, C_{6-10}-Arylamino, Thienyl, Furyl, Pyrazolyl, Thiazolyl, Isothiazolyl, Oxazolyl, Isoxazolyl, Imidazolyl, Triazolyl, Tetrazolyl, Pyridyl, Pyrimidinyl, Pyridazinyl, Chinolyl, Isochinolyl, Indolyl sowie (im Falle, daß R^1 und R^2 C_{7-12}-Aralkyl sind) C_{6-10}-Aryl und C_{7-10}-Aralkyl [wobei die Substituenten aus dieser Gruppe gegebenenfalls mit 1 bis 5 gleichen oder verschiedenen Substituenten substituiert sind, die ausgewählt sind aus Halogen, Hydroxy, C_{1-4}-Alkyl, C_{2-4}-Alkenyl, C_{2-4}-Alkinyl, C_{6-10}-Aryl, C_{1-4}-Alkoxy, Phenoxy, C_{1-4}-Alkylthio und Phenylthio];

C_{2-10}-Alkenyl, C_{2-10}-Alkinyl, C_{1-4}-Alkoxy, C_{1-4}-Alkylthio, C_{1-4}-Alkylsulfinyl, C_{1-4}-Alkylsulfonyl, Amino, Mono- oder Di-C_{1-4}-Alkylamino, C_{3-6}-Cycloalkylamino sowie (im Falle, daß R^1 und R^2 C_{7-12}-Aralkyl sind) C_{1-15}-Alkyl [wobei die Substituenten aus dieser Gruppe gegebenenfalls mit 1 bis 5 gleichen oder verschiedenen Substituenten substituiert sind, die ausgewählt sind aus Halogen, Hydroxy, C_{1-4}-Alkoxy und C_{1-4}-Alkylthio];
Nitro, Hydroxy, Mercapto, Oxo, Thioxo, Cyano, Carbamoyl, Carboxy, C_{1-4}-Alkoxycarbonyl, Sulfo, Halogen, C_{2-6}-Acylamino, C_{2-4}-Acyl und C_{6-10}-Arylcarbonyl; oder
R^1 und R^2 zusammen mit dem benachbarten Stickstoffatom eine Aziridino-, Azetidino-, Pyrrolidino-, Morpholino- oder Thiomorpholinogruppe darstellen.

8. Verfahren zur Herstellung einer Verbindung der folgenden Formel oder eines Salzes davon:



umfassend das Umsetzen einer Verbindung der folgenden Formel:



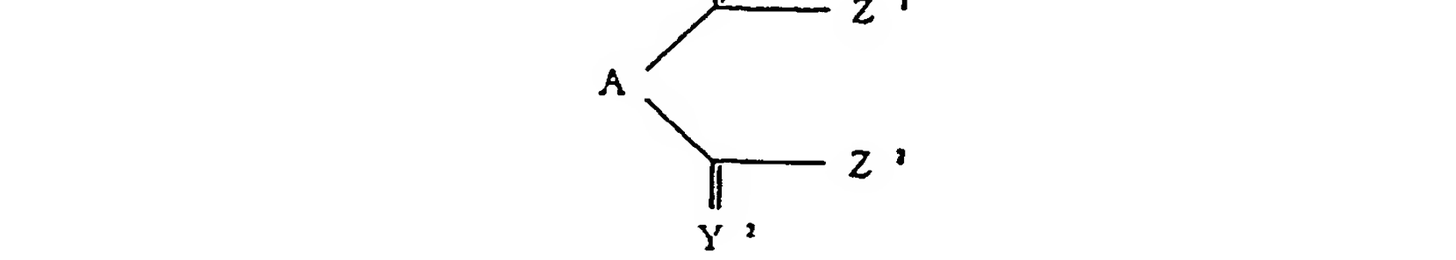
mit einer Verbindung der Formel:

$$R^3\text{-}NH(CH_2)_n\text{-}B\,,$$

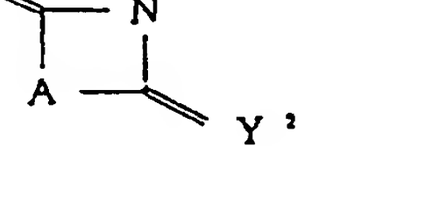
wobei R, X, Y^1, Y^2 und A dasselbe wie in Anspruch 1 bedeuten,
n 0 oder 1 ist,
B C_{3-8}-Cycloalkyl, C_{3-8}-Cycloalkenyl oder C_{6-14}-Aryl, Thienyl, Furyl, Pyrrolyl, Pyridyl, Oxazolyl, Thiazolyl, Pyrazolyl, Imidazolyl, Isoxazolyl, Isothiazolyl, Oxadiazolyl, Thiadiazolyl, Triazolyl, Tetrazolyl, N-Oxidpyridyl, Pyrimidinyl, N-Oxidpyrimidinyl, Pyridazinyl, Pyrazinyl, N-Oxidpyrazinyl, N-Oxidpyridazinyl, Benzofuryl, Benzothienyl, Benzothiazolyl, Benzoxazolyl, Triazinyl, Oxotriazinyl, Tetrazolo[1,5-b]pyridazinyl, Triazolo[4,5-b]pyridazinyl, Oxoimidazolyl, Dioxotriazinyl, Pyrrolidinyl, Piperidyl, Pyranyl, Thiopyranyl, Oxazinyl, Morpholinyl, Thiazinyl, Piperazinyl, Benzoimidazolyl, Chinolyl, Isochinolyl, Cinnolinyl, Phthalazinyl, Chinazolinyl, Chinoxalinyl, Indolizinyl, Chinolizinyl, 1,8-Naphthyridinyl, Purinyl, Pteridinyl, Dibenzofuranyl, Carbazolyl, Acridinyl, Phenanthridinyl, Phenazinyl, Phenothiazinyl und Phenoxazinyl ist, die gegebenenfalls mit einem bis fünf gleichen oder verschiedenen Substituenten substituiert sein können, die ausgewählt sind aus
C_{1-15}-Alkyl, C_{6-10}-Aryl, C_{7-10}-Aralkyl, C_{3-10}-Cycloalkyl, C_{2-10}-Alkenyl, C_{2-10}-Alkinyl, C_{3-10}-Cycloalkenyl, Nitro, Hydroxy, Mercapto, Oxo, Thioxo, Cyano, Carbamoyl, Carboxy, C_{1-4}-Alkoxycarbonyl, Sulfo, Halogen, C_{1-4}-Alkoxy, C_{6-10}-Aryloxy, C_{1-4}-Alkylthio, C_{6-10}-Arylthio, C_{1-4}-Alkylsulfinyl, C_{6-10}-Arylsulfinyl, C_{1-4}-Alkylsulfonyl, C_{6-10}-Arylsulfonyl, Amino, C_{2-6}-Acylamino, Mono- oder Di-C_{1-4}-Alkylamino, C_{3-6}-Cycloalkylamino, C_{6-10}-Arylamino, C_{2-4}-Acyl, C_{6-10}-Arylcarbonyl, Thienyl, Furyl, Pyrazolyl, Thiazolyl, Isothiazolyl, Oxazolyl, Isoxazolyl, Imidazolyl, Triazolyl, Tetrazolyl, Pyridyl, Pyrimidinyl, Pyridazinyl, Chinolyl, Isochinolyl und Indolyl; und
R^3 Wasserstoff, C_{1-10}-Alkyl (geradkettig, verzweigt oder cyclisch), C_{2-10}-Alkenyl, C_{2-10}-Alkinyl oder C_{7-12}-Aralkyl sind, die gegebenenfalls mit einem bis fünf gleichen oder verschiedenen Substituenten substituiert sein können, die ausgewählt sind aus
C_{3-10}-Cycloalkyl, C_{3-10}-Cycloalkenyl, C_{6-10}-Aryloxy, C_{6-10}-Arylthio, C_{6-10}-Arylsulfinyl, C_{6-10}-Arylsulfonyl, C_{6-10}-Arylamino, Thienyl, Furyl, Pyrazolyl, Thiazolyl, Isothiazolyl, Oxazolyl, Isoxazolyl, Imidazolyl, Triazolyl, Tetrazolyl, Pyridyl, Pyrimidinyl, Pyridazinyl, Chinolyl, Isochinolyl, Indolyl sowie (im Falle, daß R^3 C_{7-12}-Aralkyl ist) C_{6-10}-Aryl und C_{7-10}-Aralkyl [wobei die Substituenten aus dieser Gruppe gegebenenfalls mit 1 bis 5 gleichen oder verschie-

denen Substituenten substituiert sind, die ausgewählt sind aus Halogen, Hydroxy, C_{1-4}-Alkyl, C_{2-4}-Alkenyl, C_{2-4}-Alkinyl, C_{6-10}-Aryl, C_{1-4}-Alkoxy, Phenoxy, C_{1-4}-Alkylthio und Phenylthio];
C_{2-10}-Alkenyl, C_{2-10}-Alkinyl, C_{1-4}-Alkoxy, C_{1-4}-Alkylthio, C_{1-4}-Alkylsulfinyl, C_{1-4}-Alkylsulfonyl, Amino, Mono- oder Di-C_{1-4}-Alkylamino, C_{3-6}-Cycloalkylamino sowie (im Falle, daß R^3 C_{7-12}-Aralkyl ist) C_{1-15}-Alkyl [wobei die Substituenten aus dieser Gruppe gegebenenfalls mit 1 bis 5 gleichen oder verschiedenen Substituenten substituiert sind, die ausgewählt sind aus Halogen, Hydroxy, C_{1-4}-Alkoxy und C_{1-4}-Alkylthio];
Nitro, Hydroxy, Mercapto, Oxo, Thioxo, Cyano, Carbamoyl, Carboxy, C_{1-4}-Alkoxycarbonyl, Sulfo, Halogen, C_{2-6}-Acylamino, C_{2-4}-Acyl und C_{6-10}-Arylcarbonyl.

9. Verfahren zur Herstellung einer Verbindung der folgenden Formel oder eines Salzes davon:



umfassend das Umsetzen einer Verbindung der folgenden Formel:



mit einer Verbindung der folgenden Formel:

und dann das Umsetzen der entstandenen Verbindung, die die folgende Formel besitzt:

i) mit einem Amin mit der Formel:

R^1R^2NH

oder einem Salz davon mit anschließender Reaktion einer Verbindung der Formel:

R^3-$NH(CH_2)_n$-B

nach einer Acylierung, falls erforderlich, wenn R^1 ein Wasserstoffatom darstellt; oder
ii) mit einer Verbindung der Formel:

R^3-$NH(CH_2)_n$-B

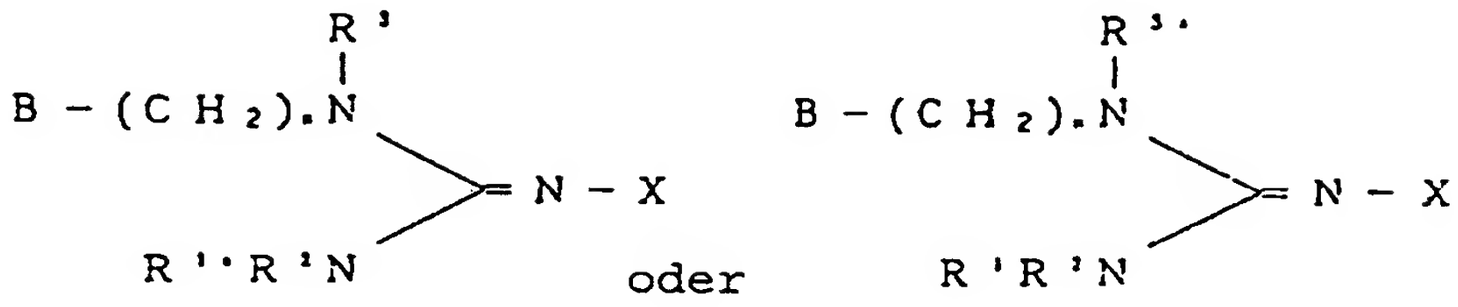
mit anschließender Reaktion eines Amin mit der Formel:

R^1R^2NH

oder eines Salzes davon nach einer Acylierung, falls erforderlich, wenn R^3 ein Wasserstoffatom darstellt;

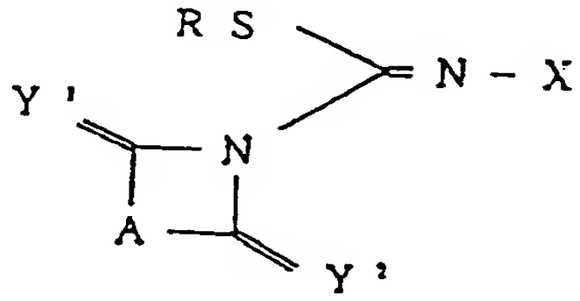
wobei A, R, X, Y^1 und Y^2 dasselbe wie in Anspruch 1 bedeuten, B, n, R^1, R^2, R^3, Z^1 und Z^2 dasselbe wie in den Ansprüchen 6, 7 und 8 bedeuten,
R^{1a} dasselbe wie R^1 bedeutet und außerdem ein C_{1-10}-Acyl (aliphatisch, alicyclisch, aromatisch oder heterocyclisch) sein kann, das gegebenenfalls mit einem bis fünf gleichen oder verschiedenen Substituenten substituiert sein kann, die ausgewählt sind aus
C_{3-10}-Cycloalkyl, C_{3-10}-Cycloalkenyl, C_{6-10}-Aryloxy, C_{6-10}-Arylthio, C_{6-10}-Arylsulfinyl, C_{6-10}-Arylsulfonyl, C_{6-10}-Arylamino, C_{6-10}-Aryl, C_{7-10}-Aralkyl, Thienyl, Furyl, Pyrazolyl, Thiazolyl, Isothiazolyl, Oxazolyl, Isoxazolyl, Imidazolyl, Triazolyl, Tetrazolyl, Pyridyl, Pyrimidinyl, Pyridazinyl, Chinolyl, Isochinolyl und Indolyl [wobei die Substituenten aus dieser Gruppe gegebenenfalls mit 1 bis 5 gleichen oder verschiedenen Substituenten substituiert sind, die ausgewählt sind aus Halogen, Hydroxy, C_{1-4}-Alkyl, C_{2-4}-Alkenyl, C_{2-4}-Alkinyl, C_{6-10}-Aryl, C_{1-4}-Alkoxy, Phenoxy, C_{1-4}-Alkylthio und Phenylthio];
C_{2-10}-Alkenyl, C_{2-10}-Alkinyl, C_{1-4}-Alkoxy, C_{1-4}-Alkylthio, C_{1-4}-Alkylsulfinyl, C_{1-4}-Alkylsulfonyl, Amino, Mono- oder Di-C_{1-4}-Alkylamino, C_{3-6}-Cycloalkylamino, C_{1-15}-Alkyl [wobei die Substituenten aus dieser Gruppe gegebenenfalls mit 1 bis 5 gleichen oder verschiedenen Substituenten substituiert sind, die ausgewählt sind aus Halogen, Hydroxy, C_{1-4}-Alkoxy und C_{1-4}-Alkylthio];
Nitro, Hydroxy, Mercapto, Oxo, Thioxo, Cyano, Carbamoyl, Carboxy, C_{1-4}-Alkoxycarbonyl, Sulfo, Halogen, C_{2-6}-Acylamino, C_{2-4}-Acyl und C_{6-10}-Arylcarbonyl; oder
R^1 und R^2 zusammen mit dem benachbarten Stickstoffatom eine cyclische Aminogruppe darstellen; und
R^{3a} dasselbe wie R^3 bedeutet und außerdem ein C_{1-10}-Acyl (aliphatisch, alicyclisch, aromatisch oder heterocyclisch) sein kann, das gegebenenfalls mit einem bis fünf gleichen oder verschiedenen Substituenten substituiert sein kann, die ausgewählt sind aus
C_{3-10}-Cycloalkyl, C_{3-10}-Cycloalkenyl, C_{6-10}-Aryloxy, C_{6-10}-Arylthio, C_{6-10}-Arylsulfinyl, C_{6-10}-Arylsulfonyl, C_{6-10}-Arylamino, C_{6-10}-Aryl, C_{7-10}-Aralkyl, Thienyl, Furyl, Pyrazolyl, Thiazolyl, Isothiazolyl, Oxazolyl, Isoxazolyl, Imidazolyl, Triazolyl, Tetrazolyl, Pyridyl, Pyrimidinyl, Pyridazinyl, Chinolyl, Isochinolyl und Indolyl [wobei die Substituenten aus dieser Gruppe gegebenenfalls mit 1 bis 5 gleichen oder verschiedenen Substituenten substituiert sind, die ausgewählt sind aus Halogen, Hydroxy, C_{1-4}-Alkyl, C_{2-4}-Alkenyl, C_{2-4}-Alkinyl, C_{6-10}-Aryl, C_{1-4}-Alkoxy, Phenoxy, C_{1-4}-Alkylthio und Phenylthio];
C_{2-10}-Alkenyl, C_{2-10}-Alkinyl, C_{1-4}-Alkoxy, C_{1-4}-Alkylthio, C_{1-4}-Alkylsulfinyl, C_{1-4}-Alkylsulfonyl, Amino, Mono- oder Di-C_{1-4}-Alkylamino, C_{3-6}-Cycloalkylamino, C_{1-15}-Alkyl [wobei die Substituenten aus dieser Gruppe gegebenenfalls mit 1 bis 5 gleichen oder verschiedenen Substituenten substituiert sind, die ausgewählt sind aus Halogen, Hydroxy, C_{1-4}-Alkoxy und C_{1-4}-Alkylthio];
Nitro, Hydroxy, Mercapto, Oxo, Thioxo, Cyano, Carbamoyl, Carboxy, C_{1-4}-Alkoxycarbonyl, Sulfo, Halogen, C_{2-6}-Acylamino, C_{2-4}-Acyl und C_{6-10}-Arylcarbonyl.

10. Verfahren zur Herstellung einer Verbindung der folgenden Formel oder eines Salzes davon:



oder

umfassend das Umsetzen einer Verbindung der folgenden Formel:



i) mit einem Amin mit der Formel:

$$R^1R^2NH$$

oder einem Salz davon mit anschließender Reaktion einer Verbindung der Formel:

$$R^3\text{-}NH(CH_2)_n\text{-}B$$

nach einer Acylierung, falls erforderlich, wenn R^1 ein Wasserstoffatom darstellt; oder
ii) mit einer Verbindung der Formel:

$$R^3\text{-}NH(CH_2)_n\text{-}B$$

mit anschließender Reaktion eines Amin mit der Formel:

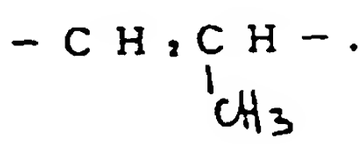
$$R^1R^2NH$$

oder eines Salzes davon nach einer Acylierung, falls erforderlich, wenn R^3 ein Wasserstoffatom darstellt;

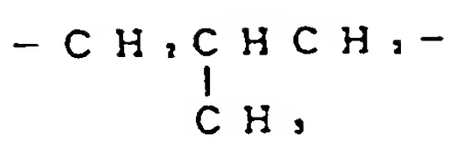
wobei A, R, X, Y^1 und Y^2 dasselbe wie in Anspruch 1 bedeuten, B, n, R^1, R^2 und R^3 dasselbe wie in den Ansprüchen 7 und 8 bedeuten und R^{1a} und R^{3a} dasselbe wie in Anspruch 9 bedeuten.

11. Verfahren gemäß einem der Ansprüche 6-10, wobei R C_{1-10}-Alkyl oder C_{7-12}-Aralkyl ist.

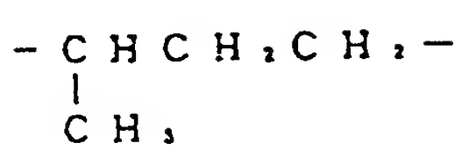
12. Verfahren gemäß einem der Ansprüche 6-10, wobei A ein C_{1-4}-Alkylen ist, das ausgewählt ist aus
$-CH_2-$, $-CH_2CH_2-$, $-CH_2CH_2CH_2-$,



$-(CH_2)_4-$,



und



13. Verfahren gemäß einem der Ansprüche 6-10, wobei A o-Phenylen, 1,2-Ethylen oder 1,3-Propylen ist.

14. Verfahren gemäß einem der Ansprüche 6-10, wobei es sich bei der elektronenziehenden Gruppe X um Cyano oder Nitro handelt.

15. Verfahren gemäß Anspruch 7 oder 10, wobei die R^1R^2N-Gruppe eine unsubstituierte Amino-, Mono-C_{1-4}-Alkylamino- oder Di-C_{1-4}-Alkylaminogruppe ist.

16. Verfahren gemäß Anspruch 9 oder 10, wobei R^{1a} C_{1-10}-Alkyl, C_{7-12}-Aralkyl, C_{1-4}-Acyl ist.

17. Verfahren gemäß Anspruch 9 oder 10, wobei die $R^{1a}R^2N$-Gruppe eine unsubstituierte Amino-, Mono-C_{1-4}-Alkylamino-, Di-C_{1-4}-Alkylamino-, C_{1-4}-Acylamino- oder N-C_{1-2}-Acyl-N-C_{1-4}-Alkylaminogruppe ist.

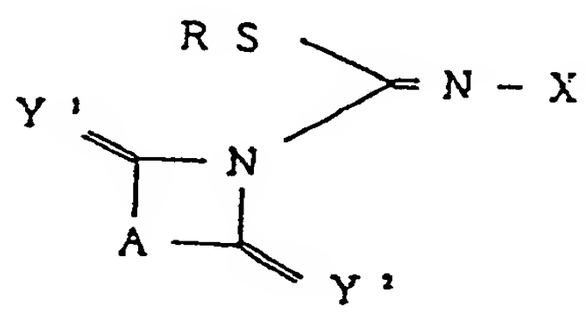
18. Verfahren gemäß einem der Ansprüche 8-10, wobei B Pyridyl und Thiazolyl ist, das mit einem oder zwei Halogenen substituiert sein kann.

19. Verfahren gemäß Anspruch 9 oder 10, wobei R^{3a} C_{1-10}-Alkyl oder C_{7-12}-Aralkyl ist.

20. Verfahren gemäß einem der Ansprüche 7, 9 oder 10, wobei die R^1R^2N-Gruppe eine unsubstituierte Amino-, Mono-C_{1-4}-Alkylamino-, Di-C_{1-4}-Alkylaminogruppe, Aziridino, Azetidino, Pyrrolidino, Morpholino oder Thiomorpholino ist.

Patentansprüche für folgenden Vertragsstaat : ES

1. Verfahren zur Herstellung einer Verbindung mit der folgenden Formel:

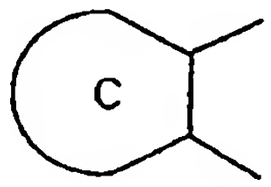


wobei

R C_{1-10}-Alkyl (geradkettig, verzweigt oder cyclisch), C_{2-10}-Alkenyl, C_{2-10}-Alkinyl, C_{7-12}-Aralkyl oder C_{1-10}-Acyl (aliphatisch, alicyclisch, aromatisch oder heterocyclisch) ist, das gegebenenfalls mit einem bis fünf gleichen oder verschiedenen Substituenten substituiert sein kann, die ausgewählt sind aus
C_{3-10}-Cycloalkyl, C_{3-10}-Cycloalkenyl, C_{6-10}-Aryloxy, C_{6-10}-Arylthio, C_{6-10}-Arylsulfinyl, C_{6-10}-Arylsulfonyl, C_{6-10}-Arylamino, Thienyl, Furyl, Pyrazolyl, Thiazolyl, Isothiazolyl, Oxazolyl, Isoxazolyl, Imidazolyl, Triazolyl, Tetrazolyl, Pyridyl, Pyrimidinyl, Pyridazinyl, Chinolyl, Isochinolyl, Indolyl sowie (im Falle, daß R C_{7-12}-Aralkyl oder C_{1-10}-Acyl ist) C_{6-10}-Aryl und C_{7-10}-Aralkyl;
C_{2-10}-Alkenyl, C_{2-10}-Alkinyl, C_{1-4}-Alkoxy, C_{1-4}-Alkylthio, C_{1-4}-Alkylsulfinyl, C_{1-4}-Alkylsulfonyl, Amino, Mono- oder Di-C_{1-4}-Alkylamino, C_{3-6}-Cycloalkylamino sowie (im Falle, daß R C_{7-12}-Aralkyl oder C_{1-10}-Acyl ist) C_{1-15}-Alkyl;
Nitro, Hydroxy, Mercapto, Oxo, Thioxo, Cyano, Carbamoyl, Carboxy, C_{1-4}-Alkoxycarbonyl, Sulfo, Halogen, C_{2-6}-Acylamino, C_{2-4}-Acyl und C_{6-10}-Arylcarbonyl;
X eine elektronenziehende Gruppe ist, die ausgewählt ist aus Cyano, Nitro, Alkoxycarbonyl, Hydroxycarbonyl, C_{6-10}-Aryloxycarbonyl, C_{1-4}-Alkylsulfonyl (gegebenenfalls mit Halogen substituiert), Sulfamoyl, Di-C_{1-4}-Alkoxy-

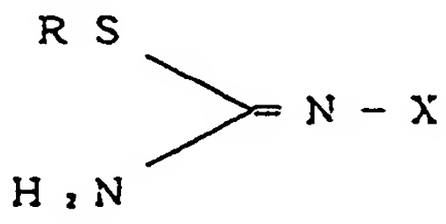
phosphoryl, C_{1-4}-Acyl (gegebenenfalls mit Halogen substituiert), Carbamoyl, C_{1-4}-Alkylsulfonylthiocarbamoyl, Thienyloxycarbonyl, Furyloxycarbonyl, Pyrazolyloxycarbonyl, Thiazolyloxycarbonyl, Isothiazolyloxycarbonyl, Oxazolyloxycarbonyl, Isoxazolyloxycarbonyl, Imidazolyloxycarbonyl, Triazolyloxycarbonyl, Tetrazolyloxycarbonyl, Pyridyloxycarbonyl, Pyrimidinyloxycarbonyl, Pyridazinyloxycarbonyl, Chinolyloxycarbonyl, Isochinolyloxycarbonyl und Indolyloxycarbonyl;

Y^1 und Y^2, die gleich oder verschieden sind, jeweils unabhängig Sauerstoff oder Schwefel sind; und
A ein zweiwertiger Kohlenwasserstoffrest ist, der ausgewählt ist aus C_{1-4}-Alkylen und einer cyclischen Gruppe, die durch die folgende Formel dargestellt wird:

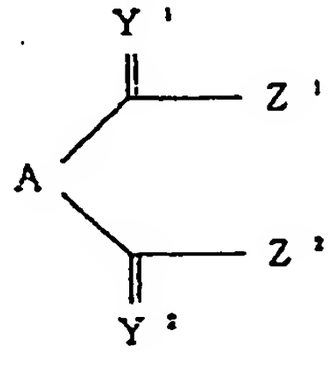


wobei der C-Ring Benzol oder Cyclohexan darstellt,

wobei das Verfahren das Umsetzen einer Verbindung der folgenden Formel:

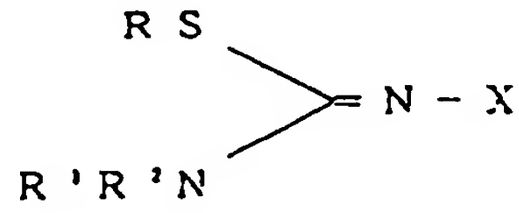


mit einer Verbindung der folgenden Formel:

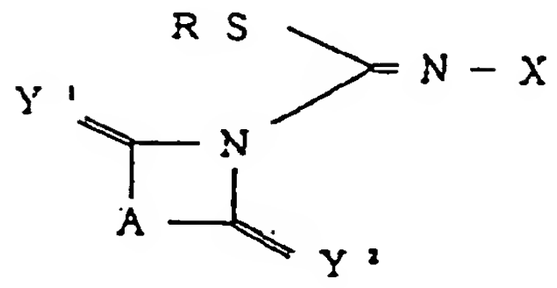


umfaßt, wobei A, R, X, Y^1 und Y^2 dasselbe wie oben bedeuten und Z^1 und Z^2, die gleich oder verschieden sind, aus Fluor, Chlor und Brom ausgewählt sind oder Z^1 und Z^2 zusammengenommen Sauerstoff darstellen.

2. Verfahren zur Herstellung einer Verbindung der folgenden Formel oder eines Salzes davon:



umfassend das Umsetzen einer Verbindung der folgenden Formel:

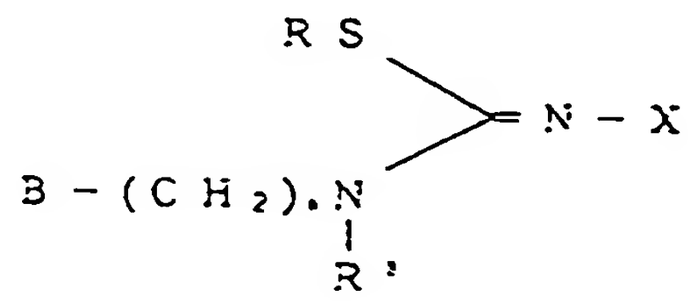


mit einer Verbindung der folgenden Formel:

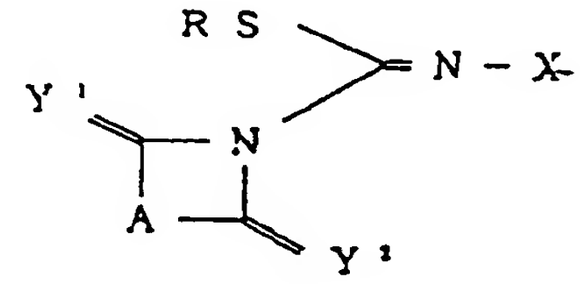
$$R^1R^2NH\,,$$

wobei A, R, X, Y^1 und Y^2 dasselbe wie in Anspruch 1 bedeuten und R^1 und R^2, die gleich oder verschieden sind, jeweils unabhängig Wasserstoff, C_{1-10}-Alkyl (geradkettig, verzweigt oder cyclisch), C_{2-10}-Alkenyl, C_{2-10}-Alkinyl oder C_{7-12}-Aralkyl sind, die gegebenenfalls mit einem bis fünf gleichen oder verschiedenen Substituenten substituiert sein können, die ausgewählt sind aus
C_{3-10}-Cycloalkyl, C_{3-10}-Cycloalkenyl, C_{6-10}-Aryloxy, C_{6-10}-Arylthio, C_{6-10}-Arylsulfinyl, C_{6-10}-Arylsulfonyl, C_{6-10}-Arylamino, Thienyl, Furyl, Pyrazolyl, Thiazolyl, Isothiazolyl, Oxazolyl, Isoxazolyl, Imidazolyl, Triazolyl, Tetrazolyl, Pyridyl, Pyrimidinyl, Pyridazinyl, Chinolyl, Isochinolyl, Indolyl sowie (im Falle, daß R^1 und R^2 C_{7-12}-Aralkyl sind) C_{6-10}-Aryl und C_{7-10}-Aralkyl [wobei die Substituenten aus dieser Gruppe gegebenenfalls mit 1 bis 5 gleichen oder verschiedenen Substituenten substituiert sind, die ausgewählt sind aus Halogen, Hydroxy, C_{1-4}-Alkyl, C_{2-4}-Alkenyl, C_{2-4}-Alkinyl, C_{6-10}-Aryl, C_{1-4}-Alkoxy, Phenoxy, C_{1-4}-Alkylthio und Phenylthio];
C_{2-10}-Alkenyl, C_{2-10}-Alkinyl, C_{1-4}-Alkoxy, C_{1-4}-Alkylthio, C_{1-4}-Alkylsulfinyl, C_{1-4}-Alkylsulfonyl, Amino, Mono- oder Di-C_{1-4}-Alkylamino, C_{3-6}-Cycloalkylamino sowie (im Falle, daß R^1 und R^2 C_{7-12}-Aralkyl sind) C_{1-15}-Alkyl [wobei die Substituenten aus dieser Gruppe gegebenenfalls mit 1 bis 5 gleichen oder verschiedenen Substituenten substituiert sind, die ausgewählt sind aus Halogen, Hydroxy, C_{1-4}-Alkoxy und C_{1-4}-Alkylthio];
Nitro, Hydroxy, Mercapto, Oxo, Thioxo, Cyano, Carbamoyl, Carboxy, C_{1-4}-Alkoxycarbonyl, Sulfo, Halogen, C_{2-6}-Acylamino, C_{2-4}-Acyl und C_{6-10}-Arylcarbonyl; oder
R^1 und R^2 zusammen mit dem benachbarten Stickstoffatom eine Aziridino-, Azetidino-, Pyrrolidino-, Morpholino- oder Thiomorpholinogruppe darstellen.

3. Verfahren zur Herstellung einer Verbindung der folgenden Formel oder eines Salzes davon:



umfassend das Umsetzen einer Verbindung der folgenden Formel:

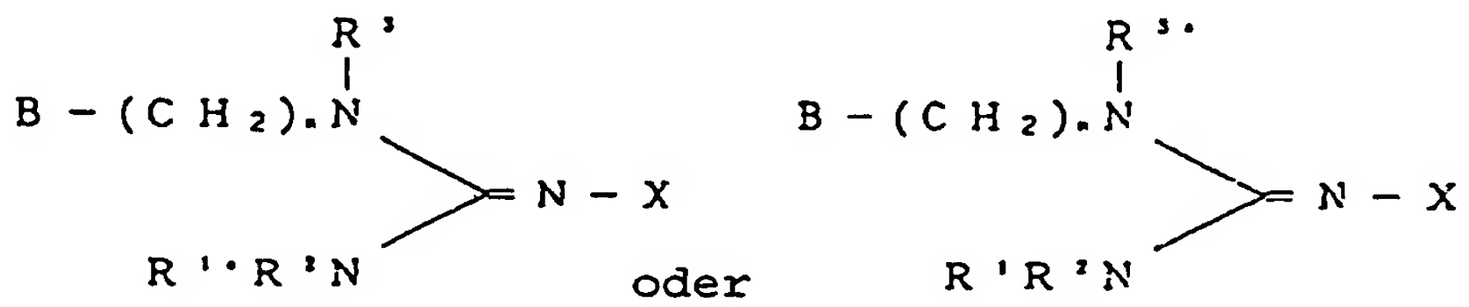


mit einer Verbindung der Formel:

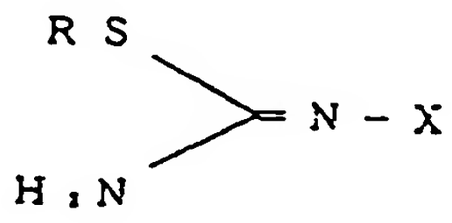
$$R^3\text{-}NH(CH_2)_n\text{-}B\,,$$

wobei R, X, Y^1, Y^2 und A dasselbe wie in Anspruch 1 bedeuten,
n 0 oder 1 ist,
B C_{3-8}-Cycloalkyl, C_{3-8}-Cycloalkenyl oder C_{6-14}-Aryl, Thienyl, Furyl, Pyrrolyl, Pyridyl, Oxazolyl, Thiazolyl, Pyrazolyl, Imidazolyl, Isoxazolyl, Isothiazolyl, Oxadiazolyl, Thiadiazolyl, Triazolyl, Tetrazolyl, N-Oxidpyridyl, Pyrimidinyl, N-Oxidpyrimidinyl, Pyridazinyl, Pyrazinyl, N-Oxidpyrazinyl, N-Oxidpyridazinyl, Benzofuryl, Benzothienyl, Benzothiazolyl, Benzoxazolyl, Triazinyl, Oxotriazinyl, Tetrazolo[1,5-b]pyridazinyl, Triazolo[4,5-b]pyridazinyl, Oxoimidazolyl, Dioxotriazinyl, Pyrrolidinyl, Piperidyl, Pyranyl, Thiopyranyl, Oxazinyl, Morpholinyl, Thiazinyl, Piperazinyl, Benzoimidazolyl, Chinolyl, Isochinolyl, Cinnolinyl, Phthalazinyl, Chinazolinyl, Chinoxalinyl, Indolizinyl, Chinolizinyl, 1,8-Naphthyridinyl, Purinyl, Pteridinyl, Dibenzofuranyl, Carbazolyl, Acridinyl, Phenanthridinyl, Phenazinyl, Phenothiazinyl und Phenoxazinyl ist, die gegebenenfalls mit einem bis fünf gleichen oder verschiedenen Substituenten substituiert sein können, die ausgewählt sind aus
C_{1-15}-Alkyl, C_{6-10}-Aryl, C_{7-10}-Aralkyl, C_{3-10}-Cycloalkyl, C_{2-10}-Alkenyl, C_{2-10}-Alkinyl, C_{3-10}-Cycloalkenyl, Nitro, Hydroxy, Mercapto, Oxo, Thioxo, Cyano, Carbamoyl, Carboxy, C_{1-4}-Alkoxycarbonyl, Sulfo, Halogen, C_{1-4}-Alkoxy, C_{6-10}-Aryloxy, C_{1-4}-Alkylthio, C_{6-10}-Arylthio, C_{1-4}-Alkylsulfinyl, C_{6-10}-Arylsulfinyl, C_{1-4}-Alkylsulfonyl, C_{6-10}-Arylsulfonyl, Amino, C_{2-6}-Acylamino, Mono- oder Di-C_{1-4}-Alkylamino, C_{3-6}-Cycloalkylamino, C_{6-10}-Arylamino, C_{2-4}-Acyl, C_{6-10}-Arylcarbonyl, Thienyl, Furyl, Pyrazolyl, Thiazolyl, Isothiazolyl, Oxazolyl, Isoxazolyl, Imidazolyl, Triazolyl, Tetrazolyl, Pyridyl, Pyrimidinyl, Pyridazinyl, Chinolyl, Isochinolyl und Indolyl; und
R^3 Wasserstoff, C_{1-10}-Alkyl (geradkettig, verzweigt oder cyclisch), C_{2-10}-Alkenyl, C_{2-10}-Alkinyl oder C_{7-12}-Aralkyl sind, die gegebenenfalls mit einem bis fünf gleichen oder verschiedenen Substituenten substituiert sein können, die ausgewählt sind aus
C_{3-10}-Cycloalkyl, C_{3-10}-Cycloalkenyl, C_{6-10}-Aryloxy, C_{6-10}-Arylthio, C_{6-10}-Arylsulfinyl, C_{6-10}-Arylsulfonyl, C_{6-10}-Arylamino, Thienyl, Furyl, Pyrazolyl, Thiazolyl, Isothiazolyl, Oxazolyl, Isoxazolyl, Imidazolyl, Triazolyl, Tetrazolyl, Pyridyl, Pyrimidinyl, Pyridazinyl, Chinolyl, Isochinolyl, Indolyl sowie (im Falle, daß R^3 C_{7-12}-Aralkyl ist) C_{6-10}-Aryl und C_{7-10}-Aralkyl [wobei die Substituenten aus dieser Gruppe gegebenenfalls mit 1 bis 5 gleichen oder verschiedenen Substituenten substituiert sind, die ausgewählt sind aus Halogen, Hydroxy, C_{1-4}-Alkyl, C_{2-4}-Alkenyl, C_{2-4}-Alkinyl, C_{6-10}-Aryl, C_{1-4}-Alkoxy, Phenoxy, C_{1-4}-Alkylthio und Phenylthio];
C_{2-10}-Alkenyl, C_{2-10}-Alkinyl, C_{1-4}-Alkoxy, C_{1-4}-Alkylthio, C_{1-4}-Alkylsulfinyl, C_{1-4}-Alkylsulfonyl, Amino, Mono- oder Di-C_{1-4}-Alkylamino, C_{3-6}-Cycloalkylamino sowie (im Falle, daß R^3 C_{7-12}-Aralkyl ist) C_{1-15}-Alkyl [wobei die Substituenten aus dieser Gruppe gegebenenfalls mit 1 bis 5 gleichen oder verschiedenen Substituenten substituiert sind, die ausgewählt sind aus Halogen, Hydroxy, C_{1-4}-Alkoxy und C_{1-4}-Alkylthio];
Nitro, Hydroxy, Mercapto, Oxo, Thioxo, Cyano, Carbamoyl, Carboxy, C_{1-4}-Alkoxycarbonyl, Sulfo, Halogen, C_{2-6}-Acylamino, C_{2-4}-Acyl und C_{6-10}-Arylcarbonyl.

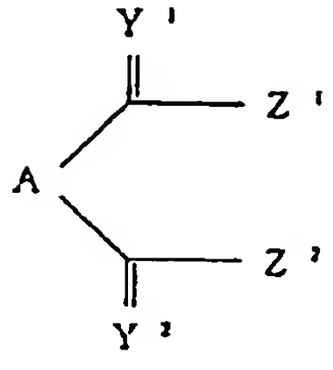
4. Verfahren zur Herstellung einer Verbindung der folgenden Formel oder eines Salzes davon:



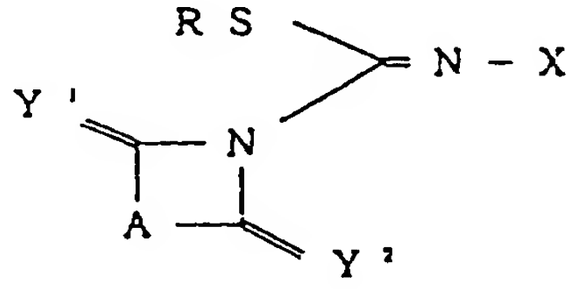
umfassend das Umsetzen einer Verbindung der folgenden Formel:



mit einer Verbindung der folgenden Formel:



und dann das Umsetzen der entstandenen Verbindung, die die folgende Formel besitzt:



i) mit einem Amin mit der Formel:

$$R^1R^2NH$$

oder einem Salz davon mit anschließender Reaktion einer Verbindung der Formel:

$$R^3\text{-}NH(CH_2)_n\text{-}B$$

nach einer Acylierung, falls erforderlich, wenn R^1 ein Wasserstoffatom darstellt; oder
ii) mit einer Verbindung der Formel:

$$R^3\text{-}NH(CH_2)_n\text{-}B$$

mit anschließender Reaktion eines Amin mit der Formel:

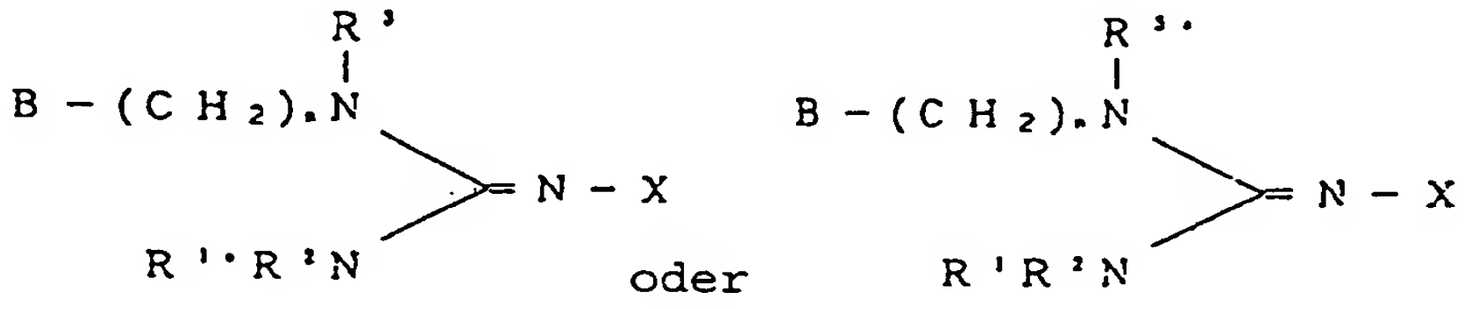
$$R^1R^2NH$$

oder eines Salzes davon nach einer Acylierung, falls erforderlich, wenn R^3 ein Wasserstoffatom darstellt;

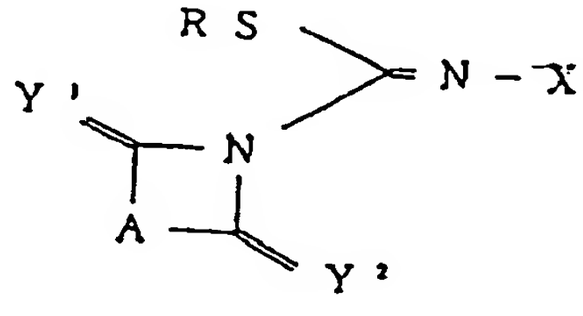
wobei A, R, X, Y^1, Y^2, Z^1 und Z^2 dasselbe wie in Anspruch 1 bedeuten, B, n, R^1, R^2 und R^3 dasselbe wie in den Ansprüchen 2 und 3 bedeuten,
R^{1a} dasselbe wie R^1 bedeutet und außerdem ein $C_{1\text{-}10}$-Acyl (aliphatisch, alicyclisch, aromatisch oder heterocyclisch) sein kann, das gegebenenfalls mit einem bis fünf gleichen oder verschiedenen Substituenten substituiert sein kann, die ausgewählt sind aus
$C_{3\text{-}10}$-Cycloalkyl, $C_{3\text{-}10}$-Cycloalkenyl, $C_{6\text{-}10}$-Aryloxy, $C_{6\text{-}10}$-Arylthio, $C_{6\text{-}10}$-Arylsulfinyl, $C_{6\text{-}10}$-Arylsulfonyl, $C_{6\text{-}10}$-Arylamino, $C_{6\text{-}10}$-Aryl, $C_{7\text{-}10}$-Aralkyl, Thienyl, Furyl, Pyrazolyl, Thiazolyl, Isothiazolyl, Oxazolyl, Isoxazolyl, Imidazolyl, Triazolyl, Tetrazolyl, Pyridyl, Pyrimidinyl, Pyridazinyl, Chinolyl, Isochinolyl und Indolyl [wobei die Substituenten aus dieser Gruppe gegebenenfalls mit 1 bis 5 gleichen oder verschiedenen Substituenten substituiert sind, die ausgewählt sind aus Halogen, Hydroxy, $C_{1\text{-}4}$-Alkyl, $C_{2\text{-}4}$-Alkenyl, $C_{2\text{-}4}$-Alkinyl, $C_{6\text{-}10}$-Aryl, $C_{1\text{-}4}$-Alkoxy, Phenoxy, $C_{1\text{-}4}$-Alkylthio und Phenylthio];
$C_{2\text{-}10}$-Alkenyl, $C_{2\text{-}10}$-Alkinyl, $C_{1\text{-}4}$-Alkoxy, $C_{1\text{-}4}$-Alkylthio, $C_{1\text{-}4}$-Alkylsulfinyl, $C_{1\text{-}4}$-Alkylsulfonyl, Amino, Mono- oder Di-$C_{1\text{-}4}$-Alkylamino, $C_{3\text{-}6}$-Cycloalkylamino, $C_{1\text{-}15}$-Alkyl [wobei die Substituenten aus dieser Gruppe gegebenenfalls mit 1 bis 5 gleichen oder verschiedenen Substituenten substituiert sind, die ausgewählt sind aus Halogen, Hydroxy, $C_{1\text{-}4}$-Alkoxy und $C_{1\text{-}4}$-Alkylthio];

Nitro, Hydroxy, Mercapto, Oxo, Thioxo, Cyano, Carbamoyl, Carboxy, C_{1-4}-Alkoxycarbonyl, Sulfo, Halogen, C_{2-6}-Acylamino, C_{2-4}-Acyl und C_{6-10}-Arylcarbonyl; oder
R^1 und R^2 zusammen mit dem benachbarten Stickstoffatom eine cyclische Aminogruppe darstellen; und
R^{3a} dasselbe wie R^3 bedeutet und außerdem ein C_{1-10}-Acyl (aliphatisch, alicyclisch, aromatisch oder heterocyclisch) sein kann, das gegebenenfalls mit einem bis fünf gleichen oder verschiedenen Substituenten substituiert sein kann, die ausgewählt sind aus
C_{3-10}-Cycloalkyl, C_{3-10}-Cycloalkenyl, C_{6-10}-Aryloxy, C_{6-10}-Arylthio, C_{6-10}-Arylsulfinyl, C_{6-10}-Arylsulfonyl, C_{6-10}-Arylamino, C_{6-10}-Aryl, C_{7-10}-Aralkyl, Thienyl, Furyl, Pyrazolyl, Thiazolyl, Isothiazolyl, Oxazolyl, Isoxazolyl, Imidazolyl, Triazolyl, Tetrazolyl, Pyridyl, Pyrimidinyl, Pyridazinyl, Chinolyl, Isochinolyl und Indolyl [wobei die Substituenten aus dieser Gruppe gegebenenfalls mit 1 bis 5 gleichen oder verschiedenen Substituenten substituiert sind, die ausgewählt sind aus Halogen, Hydroxy, C_{1-4}-Alkyl, C_{2-4}-Alkenyl, C_{2-4}-Alkinyl, C_{6-10}-Aryl, C_{1-4}-Alkoxy, Phenoxy, C_{1-4}-Alkylthio und Phenylthio];
C_{2-10}-Alkenyl, C_{2-10}-Alkinyl, C_{1-4}-Alkoxy, C_{1-4}-Alkylthio, C_{1-4}-Alkylsulfinyl, C_{1-4}-Alkylsulfonyl, Amino, Mono- oder Di-C_{1-4}-Alkylamino, C_{3-6}-Cycloalkylamino, C_{1-15}-Alkyl [wobei die Substituenten aus dieser Gruppe gegebenenfalls mit 1 bis 5 gleichen oder verschiedenen Substituenten substituiert sind, die ausgewählt sind aus Halogen, Hydroxy, C_{1-4}-Alkoxy und C_{1-4}-Alkylthio];
Nitro, Hydroxy, Mercapto, Oxo, Thioxo, Cyano, Carbamoyl, Carboxy, C_{1-4}-Alkoxycarbonyl, Sulfo, Halogen, C_{2-6}-Acylamino, C_{2-4}-Acyl und C_{6-10}-Arylcarbonyl.

5. Verfahren zur Herstellung einer Verbindung der folgenden Formel oder eines Salzes davon:



umfassend das Umsetzen einer Verbindung der folgenden Formel:



i) mit einem Amin mit der Formel:

$$R^1R^2NH$$

oder einem Salz davon mit anschließender Reaktion einer Verbindung der Formel:

$$R^3\text{-}NH(CH_2)_n\text{-}B$$

nach einer Acylierung, falls erforderlich, wenn R^1 ein Wasserstoffatom darstellt; oder
ii) mit einer Verbindung der Formel:

$$R^3\text{-}NH(CH_2)_n\text{-}B$$

mit anschließender Reaktion eines Amin mit der Formel:

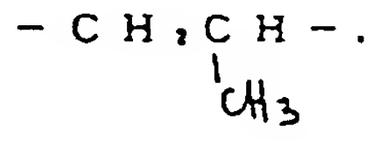
$$R^1R^2NH$$

oder eines Salzes davon nach einer Acylierung, falls erforderlich, wenn R^3 ein Wasserstoffatom darstellt;

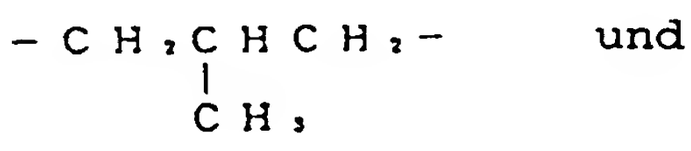
wobei A, R, X, Y^1 und Y^2 dasselbe wie in Anspruch 1 bedeuten, B, n, R^1, R^2 und R^3 dasselbe wie in den Ansprüchen 2 und 3 bedeuten und R^{1a} und R^{3a} dasselbe wie in Anspruch 4 bedeuten.

6. Verfahren gemäß einem der Ansprüche 1-5, wobei R C_{1-10}-Alkyl oder C_{7-12}-Aralkyl ist.

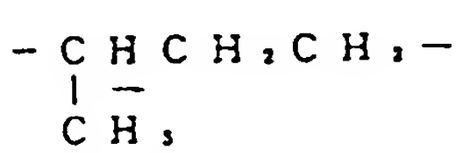
7. Verfahren gemäß einem der Ansprüche 1-5, wobei A ein C_{1-4}-Alkylen ist, das ausgewählt ist aus
$-CH_2-$, $-CH_2CH_2-$, $-CH_2CH_2CH_2-$,



$-(CH_2)_4-$,



und



8. Verfahren gemäß einem der Ansprüche 1-5, wobei A o-Phenylen, 1,2-Ethylen oder 1,3-Propylen ist.

9. Verfahren gemäß einem der Ansprüche 1-5, wobei es sich bei der elektronenziehenden Gruppe X um Cyano oder Nitro handelt.

10. Verfahren gemäß Anspruch 2 oder 5, wobei die R^1R^2N-Gruppe eine unsubstituierte Amino-, Mono-C_{1-4}-Alkylamino- oder Di-C_{1-4}-Alkylaminogruppe ist.

11. Verfahren gemäß Anspruch 4 oder 5, wobei R^{1a} C_{1-10}-Alkyl, C_{7-12}-Aralkyl, C_{1-4}-Acyl ist.

12. Verfahren gemäß Anspruch 4 oder 5, wobei die $R^{1a}R^2N$-Gruppe eine unsubstituierte Amino, Mono-C_{1-4}-Alkylamino-, Di-C_{1-4}-Alkylamino-, C_{1-4}-Acylamino- oder N-C_{1-2}-Acyl-N-C_{1-4}-Alkylaminogruppe ist.

13. Verfahren gemäß einem der Ansprüche 3-5, wobei B Pyridyl und Thiazolyl ist, das mit einem oder zwei Halogenen substituiert sein kann.

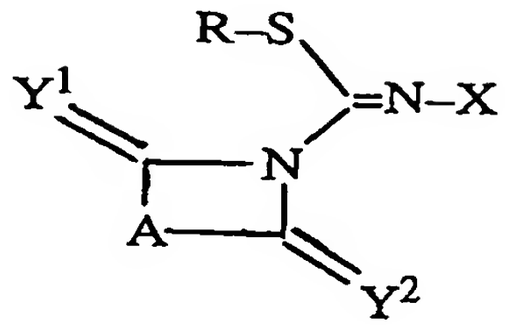
14. Verfahren gemäß Anspruch 4 oder 5, wobei R^{3a} C_{1-10}-Alkyl oder C_{7-12}-Aralkyl ist.

15. Verfahren gemäß einem der Ansprüche 2, 4 oder 5, wobei die R^1R^2N-Gruppe eine unsubstituierte Amino-, Mono-C_{1-4}-Alkylamino-, Di-C_{1-4}-Alkylaminogruppe, Aziridino, Azetidino, Pyrrolidino, Morpholino oder Thiomorpholino ist.

Revendications

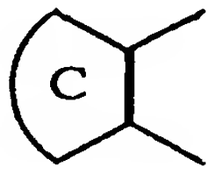
Revendications pour les Etats contractants suivants : AT, BE, CH, DE, DK, FR, GB, GR, IT, LI, LU, NL, SE

1. Composé présentant la formule suivante :



dans laquelle

R représente un groupe alkyle en C_{1-10} linéaire, ramifié ou cyclique, alcényle en C_{2-10}, alcynyle en C_{2-10}, aralkyle en C_{7-12} ou acyle en C_{1-10} aliphatique, alicyclique, aromatique ou hétérocyclique, lequel groupe peut éventuellement porter de 1 à 5 substituants identiques ou différents et choisis parmi les groupes cycloalkyle en C_{3-10}, cycloalcényle en C_{3-10}, aryloxy en C_{6-10}, arylthio en C_{6-10}, arylsulfinyle en C_{6-10}, arylsulfonyle en C_{6-10}, arylamino en C_{6-10}, thiényle, furyle, pyrazolyle, thiazolyle, isothiazolyle, oxazolyle, isoxazolyle, imidazolyle, triazolyle, tétrazolyle, pyridyle, pyrimidinyle, pyridazinyle, quinolyle, isoquinolyle, indolyle, parmi les groupes aryle en C_{6-10} et aralkyle en C_{7-10} si R représente un groupe aralkyle en C_{7-12} ou acyle en C_{1-10}, parmi les groupes alcényle en C_{2-10}, alcynyle en C_{2-10}, alcoxy en C_{1-4}, alkylthio en C_{1-4}, alkylsulfinyle en C_{1-4}, alkylsulfonyle en C_{1-4}, amino, mono(alkyle en C_{1-4})amino, di(alkyle en C_{1-4})amino, (cycloalkyle en C_{3-6})-amino, parmi les groupes alkyle en C_{1-15} si R représente un groupe aralkyle en C_{7-12} ou acyle en C_{1-10}, et parmi les groupes nitro, hydroxy, mercapto, oxo, thioxo, cyano, carbamyle, carboxy, (alcoxy en C_{1-4})carbonyle, sulfo, acylamino en C_{2-6}, acyle en C_{2-4} et (aryle en C_{6-10})carbonyle et les atomes d'halogène,
X représente un groupe électroattracteur choisi parmi les groupes cyano, nitro, alcoxycarbonyle, carboxy, (aryloxy en C_{6-10})carbonyle, alkylsulfonyle en C_{1-4} portant éventuellement des atomes d'halogène comme substituants, sulfamyle, di(alcoxy en C_{1-4})phosphoryle, acyle en C_{1-4} portant éventuellement des atomes d'halogène comme substituants, carbamyle, (alkyle en C_{1-4})sulfonylthiocarbamyle, thiényloxy carbonyle, furyloxycarbonyle, pyrazolyloxycarbonyle, thiazolyloxycarbonyle, isothiazolyloxycarbonyle, oxazolyloxycarbonyle, isoxazolyloxycarbonyle, imidazolyloxycarbonyle, triazolyloxycarbonyle, tétrazolyloxycarbonyle, pyridyloxycarbonyle, pyrimidinyloxycarbonyle, pyridazinyloxycarbonyle, quinolyloxycarbonyle, isoquinolyloxycarbonyle et indolyloxycarbonyle,
Y^1 et Y^2, qui peuvent être identiques ou différents, représentent chacun, indépendamment, un atome d'oxygène ou de soufre, et
A représente un groupe hydrocarboné divalent, choisi parmi les groupes alkylène en C_{1-4} et les groupes cycliques représentés par la formule suivante



où le cycle C représente un cycle benzénique ou cyclohexanique.

2. Composé conforme à la revendication 1, dans lequel R représente un groupe alkyle en C_{1-10} ou aralkyle en C_{7-12}.

3. Composé conforme à la revendication 1, dans lequel A représente un groupe alkylène en C_{1-4} choisi parmi les suivants :

$-CH_2-$, $-CH_2CH_2-$, $-CH_2CH_2CH_2-$, $-(CH_2)_4-$,

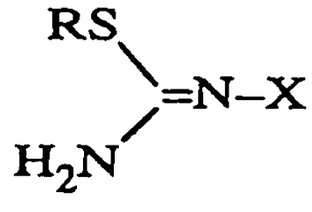
$$-CH_2-\underset{CH_3}{CH}-,\ -CH_2\,\underset{CH_3}{CH}CH_2-\ \text{et}\ -\underset{CH_3}{CH}-CH_2\,CH_2-.$$

4. Composé conforme à la revendication 1, dans lequel A représente un groupe o-phénylène, 1,2-éthylène ou 1,3-

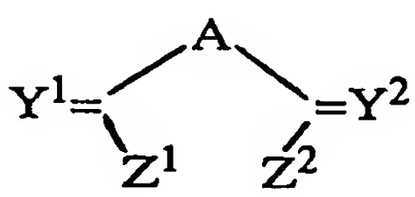
propylène.

5. Composé conforme à la revendication 1, dans lequel le groupe électroattracteur X est un groupe cyano ou nitro.

6. Procédé de préparation d'un composé conforme à la revendication 1, qui comporte le fait de faire réagir un composé de formule

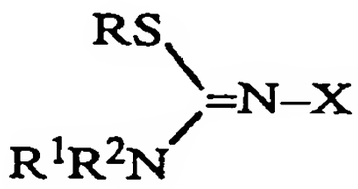


avec un composé de formule

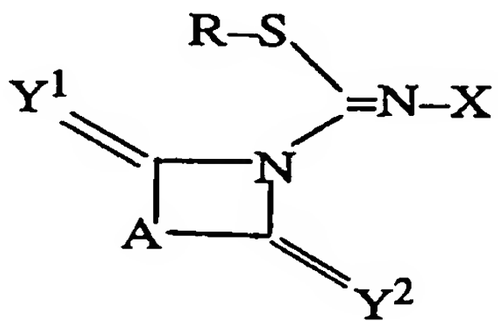


où A, R, X, Y^1 et Y^2 ont les mêmes significations que celles indiquées dans la revendication 1, et
Z^1 et Z^2, qui peuvent être identiques ou différents, représentent des atomes de fluor, de chlore ou de brome, ou bien, considérés conjointement, représentent un atome d'oxygène.

7. Procédé de préparation d'un composé de formule suivante, ou de l'un de ses sels,



qui comporte le fait de faire réagir un composé de formule



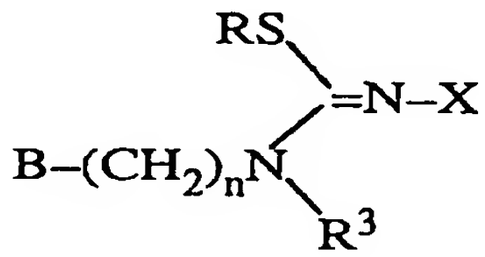
avec un composé de formule

$$R^1R^2NH$$

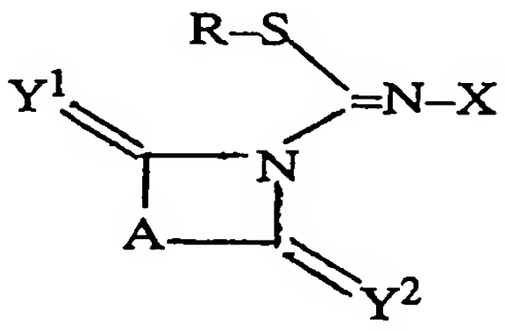
où A, R, X, Y^1 et Y^2 ont les mêmes significations que celles indiquées dans la revendication 1, et
R^1 et R^2, qui peuvent être identiques ou différents, représentent chacun, indépendamment, un atome d'hydrogène ou un groupe alkyle en C_{1-10} linéaire, ramifié ou cyclique, alcényle en C_{2-10}, alcynyle en C_{2-10} ou aralkyle en C_{7-12}, lequel groupe peut éventuellement porter de 1 à 5 substituants identiques ou différents et choisis parmi les groupes cycloalkyle en C_{3-10}, cycloalcényle en C_{3-10}, aryloxy en C_{6-10}, arylthio en C_{6-10}, arylsulfinyle en C_{6-10}, arylsulfonyle en C_{6-10}, arylamino en C_{6-10}, thiényle, furyle, pyrazolyle, thiazolyle, isothiazolyle, oxazolyle, isoxazolyle, imidazolyle, triazolyle, tétrazolyle, pyridyle, pyrimidinyle, pyridazinyle, quinolyle, isoquinolyle, indolyle, parmi les groupes aryle en C_{6-10} et aralkyle en C_{7-10} si R^1 ou R^2 représente un groupe aralkyle en C_{7-12} (ces groupes substituants portant eux-mêmes éventuellement de 1 à 5 substituants identiques ou différents et choisis parmi les atomes d'halogène et les groupes hydroxy, alkyle en C_{1-4}, alcényle en C_{2-4}, alcynyle en C_{2-4}, aryle en C_{6-10}, alcoxy

en C_{1-4}, phénoxy, alkylthio en C_{1-4} et phénylthio), parmi les groupes alcényle en C_{2-10}, alcynyle en C_{2-10}, alcoxy en C_{1-4}, alkylthio en C_{1-4}, alkylsulfinyle en C_{1-4}, alkylsulfonyle en C_{1-4}, amino, mono(alkyle en C_{1-4})amino, di(alkyle en C_{1-4})amino, (cycloalkyle en C_{3-6})amino, parmi les groupes alkyle en C_{1-15} si R^1 ou R^2 représente un groupe aralkyle en C_{7-12} (ces groupes substituants portant eux-mêmes éventuellement de 1 à 5 substituants identiques ou différents et choisis parmi les atomes d'halogène et les groupes hydroxy, alcoxy en C_{1-4} et alkylthio en C_{1-4}), et parmi les groupes nitro, hydroxy, mercapto, oxo, thioxo, cyano, carbamyle, carboxy, (alcoxy en C_{1-4})carbonyle, sulfo, acylamino en C_{2-6}, acyle en C_{2-4} et (aryle en C_{6-10})carbonyle et les atomes d'halogène,
ou bien R^1 et R^2 représentent, conjointement avec l'atome d'azote voisin, un groupe aziridino, azétidino, pyrrolidino, morpholino ou thiomorpholino.

8. Procédé de préparation d'un composé de formule suivante, ou de l'un de ses sels,



qui comporte le fait de faire réagir un composé de formule



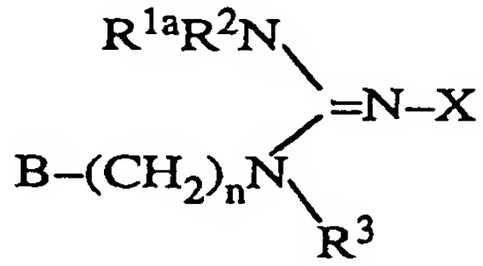
avec un composé de formule

$$R^3\text{-}NH(CH_2)_nB$$

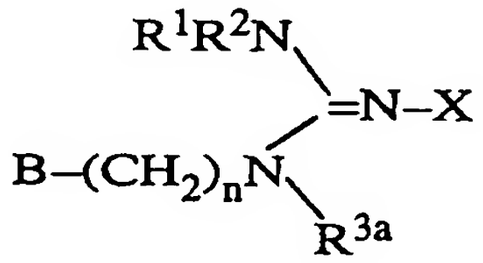
où A, R, X, Y^1 et Y^2 ont les mêmes significations que celles indiquées dans la revendication 1,
n vaut 0 ou 1,
B représente un groupe cycloalkyle en C_{3-8}, cycloalcényle en C_{3-8}, aryle en C_{6-14}, thiényle, furyle, pyrrolyle, pyridyle, oxazolyle, thiazolyle, pyrazolyle, imidazolyle, isoxazolyle, isothiazolyle, oxadiazolyle, thiadiazolyle, triazolyle, tétrazolyle, N-oxy-pyridyle, pyrimidinyle, N-oxy-pyrimidinyle, pyridazinyle, pyrazinyle, N-oxy-pyrazinyle, N-oxy-pyridazinyle, benzofuryle, benzothiényle, berizothiazolyle, benzoxazolyle, triazinyle, oxo-triazinyle, tétrazolo[1,5-b]pyridazinyle, triazolo[4,5-b]pyridazinyle, oxo-imidazolyle, dioxo-triazinyle, pyrrolidinyle, pipéridyle, pyranyle, thiopyranyle, oxazinyle, morpholinyle, thiazinyle, pipérazinyle, benzoimidazolyle, quinolyle, isoquinolyle, cinnolinyle, phtalazinyle, quinazolinyle, quinoxalinyle, indolizinylè, quinolizinyle, 1,8-naphtyridinyle, purinyle, ptéridinyle, dibenzofuranyle, carbazolyle, acridinyle, phénanthridinyle, phénazinyle, phénothiazinyle ou phénoxazinyle, qui peut éventuellement porter de 1 à 5 substituants choisis parmi les atomes d'halogène et les groupes alkyle en C_{1-15}, aryle en C_{6-10}, aralkyle en C_{7-10}, cycloalkyle en C_{3-10}, alcényle en C_{2-10}, alcynyle en C_{2-10}, cycloalcényle en C_{3-10}, nitro, hydroxy, mercapto, oxo, thioxo, cyano, carbamyle, carboxy, (alcoxy en C_{1-4})carbonyle, sulfo, alcoxy en C_{1-4}, aryloxy en C_{6-10}, alkylthio en C_{1-4}, arylthio en c_{6-10}, alkylsulfinyle en C_{1-4}, arylsulfinyle en C_{6-10}, alkylsulfonyle en c_{1-4}, arylsulfonyle en C_{6-10}, amino, acylamino en C_{2-6}, mono(alkyle en C_{1-4})amino, di(alkyle en C_{1-4})amino, (cycloalkyle en C_{3-6})amino, arylamino en C_{6-10}, acyle en C_{2-4}, (aryle en C_{6-10})carbonyle, thiényle, furyle, pyrazolyle, thiazolyle, isothiazolyle, oxazolyle, isoxazolyle, imidazolyle, triazolyle, tétrazolyle, pyridyle, pyrimidinyle, pyridazinyle, quinolyle, isoquinolyle et indolyle, et
R^3 représente un atome d'hydrogène ou un groupe alkyle en C_{1-10} linéaire, ramifié ou cyclique, alcényle en C_{2-10}, alcynyle en C_{2-10} ou aralkyle en C_{7-12}, lequel groupe peut éventuellement porter de 1 à 5 substituants identiques ou différents et choisis parmi les groupes cycloalkyle en C_{3-10}, cycloalcényle en C_{3-10}, aryloxy en C_{6-10}, arylthio en C_{6-10}, arylsulfinyle en C_{6-10}, arylsulfonyle en C_{6-10}, arylamino en C_{6-10}, thiényle, furyle, pyrazolyle, thiazolyle, isothiazolyle, oxazolyle, isoxazolyle, imidazolyle, triazolyle, tétrazolyle, pyridyle, pyrimidinyle, pyridazinyle, quinolyle,

isoquinolyle, indolyle, parmi les groupes aryle en C_{6-10} et aralkyle en C_{7-10} si R^3 représente un groupe aralkyle en C_{7-12} (ces groupes substituants portant eux-mêmes éventuellement de 1 à 5 substituants identiques ou différents et choisis parmi les atomes d'halogène et les groupes hydroxy, alkyle en C_{1-4}, alcényle en C_{2-4}, alcynyle en C_{2-4}, aryle en C_{6-10}, alcoxy en C_{1-4}, phénoxy, alkylthio en C_{1-4} et phénylthio), parmi les groupes alcényle en C_{2-10}, alcynyle en C_{2-10}, alcoxy en C_{1-4}, alkylthio en C_{1-4}, alkylsulfinyle en C_{1-4}, alkylsulfonyle en C_{1-4}, amino, mono(alkyle en C_{1-4})amino, di(alkyle en C_{1-4})amino, (cycloalkyle en C_{3-6})amino, parmi les groupes alkyle en C_{1-15} si R^3 représente un groupe aralkyle en C_{7-12}, (ces groupes substituants portant eux-mêmes éventuellement de 1 à 5 substituants identiques ou différents et choisis parmi les atomes d'halogène et les groupes hydroxy, alcoxy en C_{1-4} et alkylthio en C_{1-4}), et parmi les groupes nitro, hydroxy, mercapto, oxo, thioxo, cyano, carbamyle, carboxy, (alcoxy en C_{1-4})carbonyle, sulfo, acylamino en C_{2-6}, acyle en C_{2-4} et (aryle en C_{6-10})carbonyle et les atomes d'halogène.

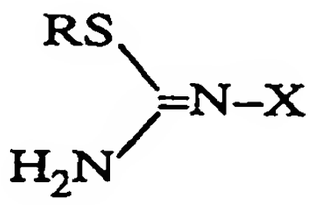
9. Procédé de préparation d'un composé de formule suivante, ou de l'un de ses sels,



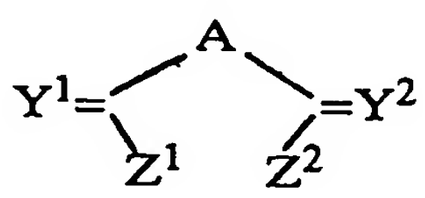
ou



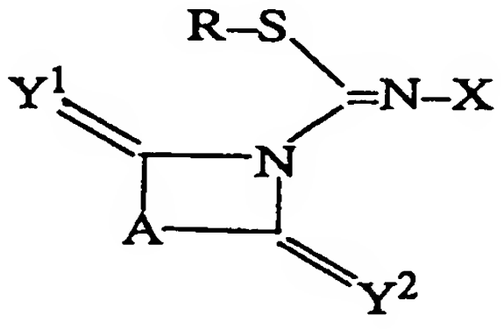
qui comporte le fait de faire réagir un composé de formule



avec un composé de formule



et le fait de faire ensuite réagir le composé ainsi obtenu, de formule



1) avec une amine de formule

$$R^1R^2NH$$

ou avec un sel d'une telle amine, puis avec un composé de formule

$$R^3\text{-}NH(CH_2)_n\text{-}B$$

après acylation, si nécessaire, quand R^1 représente un atome d'hydrogène, ou bien
2) avec un composé de formule

$$R^3\text{-}NH(CH_2)_n\text{-}B$$

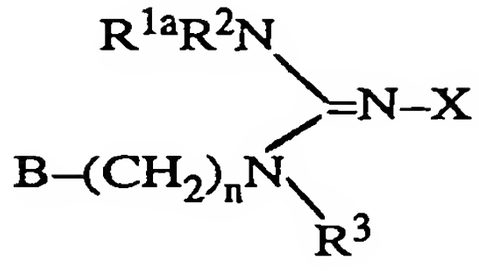
puis avec une amine de formule

$$R^1R^2NH$$

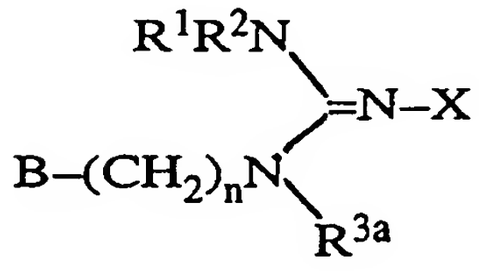
ou avec un sel d'une telle amine,

après acylation, si nécessaire, quand R^3 représente un atome d'hydrogène,
où A, R, X, Y^1 et Y^2 ont les mêmes significations que celles indiquées dans la revendication 1,
B, n, R^1, R^2, R^3, Z^1 et Z^2 ont les mêmes significations que celles indiquées dans les revendications 6, 7 et 8,
R^{1a} a la même signification que R^1, mais peut en outre représenter un groupe acyle en $C_{1\text{-}10}$ aliphatique, alicyclique, aromatique ou hétérocyclique, lequel groupe peut éventuellement porter de 1 à 5 substituants identiques ou différents et choisis parmi les groupes cycloalkyle en $C_{3\text{-}10}$, cycloalcényle en $C_{3\text{-}10}$, aryloxy en $C_{6\text{-}10}$, arylthio en $C_{6\text{-}10}$, arylsulfinyle en $C_{6\text{-}10}$, arylsulfonyle en $C_{6\text{-}10}$, arylamino en $C_{6\text{-}10}$, aryle en $C_{6\text{-}10}$, aralkyle en $C_{7\text{-}10}$, thiényle, furyle, pyrazolyle, thiazolyle, isothiazolyle, oxazolyle, isoxazolyle, imidazolyle, triazolyle, tétrazolyle, pyridyle, pyrimidinyle, pyridazinyle, quinolyle, isoquinolyle, indolyle, (ces groupes substituants portant eux-mêmes éventuellement de 1 à 5 substituants identiques ou différents et choisis parmi les atomes d'halogène et les groupes hydroxy, alkyle en $C_{1\text{-}4}$, alcényle en $C_{2\text{-}4}$, alcynyle en $C_{2\text{-}4}$, aryle en $C_{6\text{-}10}$, alcoxy en $C_{1\text{-}4}$, phénoxy, alkylthio en $C_{1\text{-}4}$ et phénylthio), alcényle en $C_{2\text{-}10}$, alcynyle en $C_{2\text{-}10}$, alcoxy en $C_{1\text{-}4}$, alkylthio en $C_{1\text{-}4}$, alkylsulfinyle en $C_{1\text{-}4}$, alkylsulfonyle en $C_{1\text{-}4}$, amino, mono(alkyle en $C_{1\text{-}4}$)amino, di(alkyle en $C_{1\text{-}4}$)amino, (cycloalkyle en $C_{3\text{-}6}$)amino, alkyle en $C_{1\text{-}15}$ (ces groupes substituants portant eux-mêmes éventuellement de 1 à 5 substituants identiques ou différents et choisis parmi les atomes d'halogène et les groupes hydroxy, alcoxy en $C_{1\text{-}4}$ et alkylthio en $C_{1\text{-}4}$), nitro, hydroxy, mercapto, oxo, thioxo, cyano, carbamyle, carboxy, (alcoxy en $C_{1\text{-}4}$)carbonyle, sulfo, acylamino en $C_{2\text{-}6}$, acyle en $C_{2\text{-}4}$ et (aryle en $C_{6\text{-}10}$)carbonyle et les atomes d'halogène,
ou bien R^{1a} et R^2 représentent, conjointement avec l'atome d'azote voisin, un groupe amino cyclique, et
R^{3a} a la même signification que R^3, mais peut en outre représenter un groupe acyle en $C_{1\text{-}10}$ aliphatique, alicyclique, aromatique ou hétérocyclique, lequel groupe peut éventuellement porter de 1 à 5 substituants identiques ou différents et choisis parmi les groupes cycloalkyle en $C_{3\text{-}10}$, cycloalcényle en $C_{3\text{-}10}$, aryloxy en $C_{6\text{-}10}$, arylthio en $C_{6\text{-}10}$, arylsulfinyle en $C_{6\text{-}10}$, arylsulfonyle en $C_{6\text{-}10}$, arylamino en $C_{6\text{-}10}$, aryle en $C_{6\text{-}10}$, aralkyle en $C_{7\text{-}10}$, thiényle, furyle, pyrazolyle, thiazolyle, isothiazolyle, oxazolyle, isoxazolyle, imidazolyle, triazolyle, tétrazolyle, pyridyle, pyrimidinyle, pyridazinyle, quinolyle, isoquinolyle, indolyle, (ces groupes substituants portant eux-mêmes éventuellement de 1 à 5 substituants identiques ou différents et choisis parmi les atomes d'halogène et les groupes hydroxy, alkyle en $C_{1\text{-}4}$, alcényle en $C_{2\text{-}4}$, alcynyle en $C_{2\text{-}4}$, aryle en $C_{6\text{-}10}$, alcoxy en $C_{1\text{-}4}$, phénoxy, alkylthio en $C_{1\text{-}4}$ et phénylthio), alcényle en $C_{2\text{-}10}$, alcynyle en $C_{2\text{-}10}$, alcoxy en $C_{1\text{-}4}$, alkylthio en $C_{1\text{-}4}$, alkylsulfinyle en $C_{1\text{-}4}$, alkylsulfonyle en $C_{1\text{-}4}$, amino, mono(alkyle en $C_{1\text{-}4}$)amino, di(alkyle en $C_{1\text{-}4}$)amino, (cycloalkyle en $C_{3\text{-}6}$)amino, alkyle en $C_{1\text{-}15}$ (ces groupes substituants portant eux-mêmes éventuellement de 1 à 5 substituants identiques ou différents et choisis parmi les atomes d'halogène et les groupes hydroxy, alcoxy en $C_{1\text{-}4}$ et alkylthio en $C_{1\text{-}4}$), nitro, hydroxy, mercapto, oxo, thioxo, cyano, carbamyle, carboxy, (alcoxy en $C_{1\text{-}4}$)carbonyle, sulfo, acylamino en $C_{2\text{-}6}$, acyle en $C_{2\text{-}4}$ et (aryle en $C_{6\text{-}10}$)carbonyle et les atomes d'halogène.

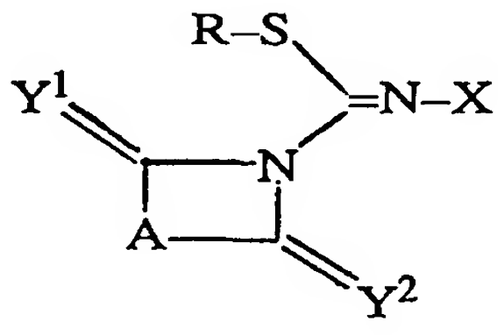
10. Procédé de préparation d'un composé de formule suivante, ou de l'un de ses sels,



ou



qui comporte le fait de faire réagir un composé de formule



1) avec une amine de formule

$$R^1R^2NH$$

ou avec un sel d'une telle amine, puis avec un composé de formule

$$R^3\text{-}NH(CH_2)_n\text{-}B$$

après acylation, si nécessaire, quand R^1 représente un atome d'hydrogène, ou bien

2) avec un composé de formule

$$R^3\text{-}NH(CH_2)_n\text{-}B$$

puis avec une amine de formule

$$R^1R^2NH$$

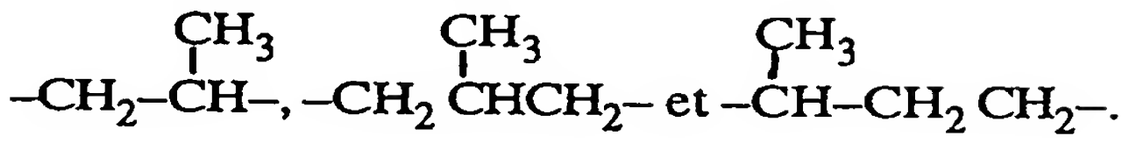
ou avec un sel d'une telle amine,

après acylation, si nécessaire, quand R^3 représente un atome d'hydrogène,
où A, R, X, Y^1 et Y^2 ont les mêmes significations que celles indiquées dans la revendication 1,
B, n, R^1, R^2 et R^3 ont les mêmes significations que celles indiquées dans les revendications 7 et 8, et
R^{1a} et R^{3a} ont les mêmes significations-que celles indiquées dans la revendication 9.

11. Procédé conforme à l'une des revendications 6 à 10, dans lequel R représente un groupe alkyle en $C_{1\text{-}10}$ ou aralkyle en $C_{7\text{-}12}$.

12. Procédé conforme à l'une des revendications 6 à 10, dans lequel A représente un groupe alkylène en $C_{1\text{-}4}$ choisi parmi les suivants :

$-CH_2-$, $-CH_2CH_2-$, $-CH_2CH_2CH_2-$, $-(CH_2)_4-$,



13. Procédé conforme à l'une des revendications 6 à 10, dans lequel A représente un groupe o-phénylène, 1,2-éthylène ou 1,3-propylène.

14. Procédé conforme à l'une des revendications 6 à 10, dans lequel le groupe électroattracteur X est un groupe cyano ou nitro.

15. Procédé conforme à la revendication 7 ou 10, dans lequel ledit groupe R^1R^2N est un groupe amino sans substituants, mono(alkyle en C_{1-4})amino ou di(alkyle en C_{1-4})amino.

16. Procédé conforme à la revendication 9 ou 10, dans lequel R^{1a} représente un groupe alkyle en C_{1-10}, aralkyle en C_{7-12} ou acyle en C_{1-4}.

17. Procédé conforme à la revendication 9 ou 10, dans lequel ledit groupe $R^{1a}R^2N$ est un groupe amino sans substituants, mono-(alkyle en C_{1-4})amino, di(alkyle en C_{1-4})amino, (acyle en C_{1-4})amino ou N-(acyle en C_{1-2})-N-(alkyle en C_{1-4})amino.

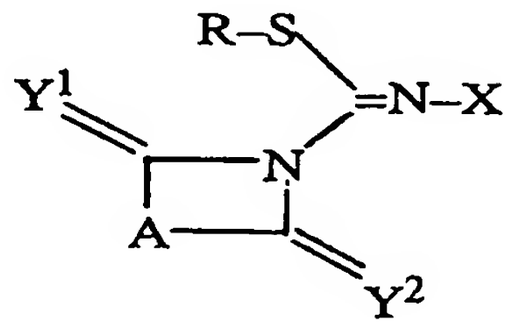
18. Procédé conforme à l'une des revendications 8 à 10, dans lequel B représente un groupe pyridyle ou thiazolyle qui peut porter un ou deux atomes d'halogène en tant que substituants.

19. Procédé conforme à la revendication 9 ou 10, dans lequel R^{3a} représente un groupe alkyle en C_{1-10} ou aralkyle en C_{7-12}.

20. Procédé conforme à la revendication 7, 9 ou 10, dans lequel ledit groupe R^1R^2N est un groupe amino sans substituants, mono(alkyle en C_{1-4})amino, di(alkyle en C_{1-4})amino, aziridino, azétidino, pyrrolidino, morpholino ou thiomorpholino.

Revendications pour l'Etat contractant suivant : ES

1. Procédé de préparation d'un composé présentant la formule suivante :



dans laquelle

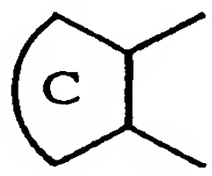
R représente un groupe alkyle en C_{1-10} linéaire, ramifié ou cyclique, alcényle en C_{2-10}, alcynyle en C_{2-10}, aralkyle en C_{7-12} ou acyle en C_{1-10} aliphatique, alicyclique, aromatique ou hétérocyclique, lequel groupe peut éventuellement porter de 1 à 5 substituants identiques ou différents et choisis parmi les groupes cycloalkyle en C_{3-10}, cycloalcényle en C_{3-10}, aryloxy en C_{6-10}, arylthio en C_{6-10}, arylsulfinyle en C_{6-10}, arylsulfonyle en C_{6-10}, arylamino en C_{6-10}, thiényle, furyle, pyrazolyle, thiazolyle, isothiazolyle, oxazolyle, isoxazolyle, imidazolyle, triazolyle, tétrazolyle, pyridyle, pyrimidinyle, pyridazinyle, quinolyle, isoquinolyle, indolyle, parmi les groupes aryle en C_{6-10} et aralkyle en C_{7-10} si R représente un groupe aralkyle en C_{7-12} ou acyle en C_{1-10}, parmi les groupes alcényle en C_{2-10}, alcynyle en C_{2-10}, alcoxy en C_{1-4}, alkylthio en C_{1-4}, alkylsulfinyle en C_{1-4}, alkylsul-

fonyle en C_{1-4}, amino, mono(alkyle en C_{1-4})amino, di(alkyle en C_{1-4})amino, (cycloalkyle en C_{3-6})amino, parmi les groupes alkyle en C_{1-15} si R représente un groupe aralkyle en C_{7-12} ou acyle en c_{1-10}, et parmi les groupes nitro, hydroxy, mercapto, oxo, thioxo, cyano, carbamyle, carboxy, (alcoxy en C_{1-4})carbonyle, sulfo, acylamino en C_{2-6}, acyle en C_{2-4} et (aryle en C_{6-10})carbonyle et les atomes d'halogène,

X représente un groupe électroattracteur choisi parmi les groupes cyano, nitro, alcoxycarbonyle, carboxy, (aryloxy en C_{6-10})carbonyle, alkylsulfonyle en C_{1-4} portant éventuellement des atomes d'halogène comme substituants, sulfamyle, di(alcoxy en C_{1-4})phosphoryle, acyle en C_{1-4} portant éventuellement des atomes d'halogène comme substituants, carbamyle, (alkyle en C_{1-4})sulfonylthiocarbamyle, thiényloxycarbonyle, furyloxycarbonyle, pyrazolyloxycarbonyle, thiazolyloxycarbonyle, isothiazolyloxycarbonyle, oxazolyloxycarbonyle, isoxazolyloxycarbonyle, imidazolyloxycarbonyle, triazolyloxycarbonyle, tétrazolyloxycarbonyle, pyridyloxycarbonyle, pyrimidinyloxycarbonyle, pyridazinyloxycarbonyle, quinolyloxycarbonyle, isoquinolyloxycarbonyle et indolyloxycarbonyle,

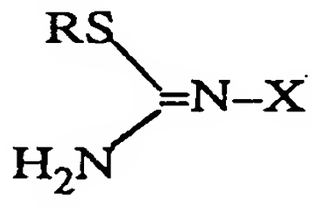
Y^1 et Y^2, qui peuvent être identiques ou différents, représentent chacun, indépendamment, un atome d'oxygène ou de soufre, et

A représente un groupe hydrocarboné divalent, choisi parmi les groupes alkylène en C_{1-4} et les groupes cycliques représentés par la formule suivante

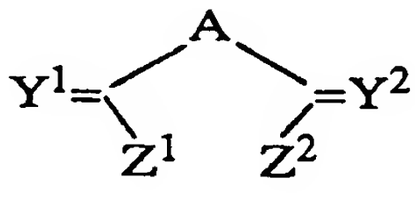


où le cycle C représente un cycle benzénique ou cyclohexanique,

lequel procédé comporte le fait de faire réagir un composé de formule

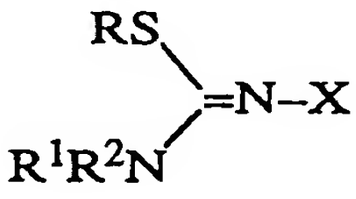


avec un composé de formule

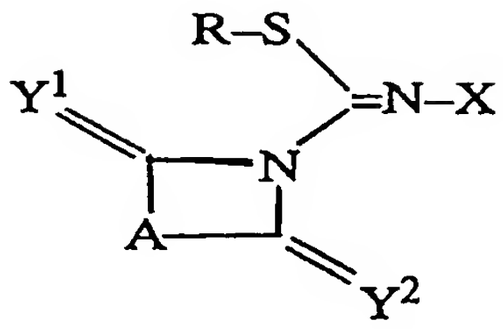


où A, R, X, Y^1 et Y^2 ont les mêmes significations que celles indiquées ci-dessus, et
Z^1 et Z^2, qui peuvent être identiques ou différents, représentent des atomes de fluor, de chlore ou de brome, ou bien, considérés conjointement, représentent un atome d'oxygène.

2. Procédé de préparation d'un composé de formule suivante, ou de l'un de ses sels,



qui comporte le fait de faire réagir un composé de formule

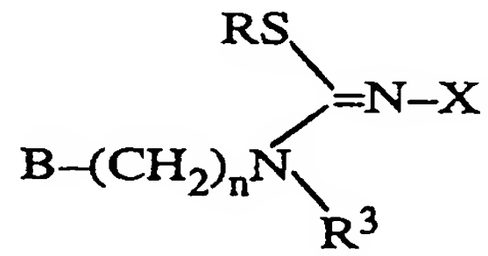


avec un composé de formule

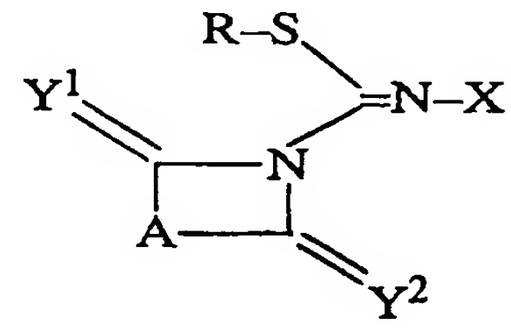
R^1R^2NH

où A, R, X, Y^1 et Y^2 ont les mêmes significations que celles indiquées dans la revendication 1, et
R^1 et R^2, qui peuvent être identiques ou différents, représentent chacun, indépendamment, un atome d'hydrogène ou un groupe alkyle en C_{1-10} linéaire, ramifié ou cyclique, alcényle en C_{2-10}, alcynyle en C_{2-10} ou aralkyle en C_{7-12}, lequel groupe peut éventuellement porter de 1 à 5 substituants identiques ou différents et choisis parmi les groupes cycloalkyle en C_{3-10}, cycloalcényle en C_{3-10}, aryloxy en C_{6-10}, arylthio en C_{6-10}, arylsulfinyle en C_{6-10}, arylsulfonyle en C_{6-10}, arylamino en C_{6-10}, thiényle, furyle, pyrazolyle, thiazolyle, isothiazolyle, oxazolyle, isoxazolyle, imidazolyle, triazolyle, tétrazolyle, pyridyle, pyrimidinyle, pyridazinyle, quinolyle, isoquinolyle, indolyle, parmi les groupes aryle en C_{6-10} et aralkyle en C_{7-10} si R^1 ou R^2 représente un groupe aralkyle en C_{7-12} (ces groupes substituants portant eux-mêmes éventuellement de 1 à 5 substituants identiques ou différents et choisis parmi les atomes d'halogène et les groupes hydroxy, alkyle en C_{1-4}, alcényle en C_{2-4}, alcynyle en C_{2-4}, aryle en C_{6-10}, alcoxy en C_{1-4}, phénoxy, alkylthio en C_{1-4} et phénylthio), parmi les groupes alcényle en C_{2-10}, alcynyle en C_{2-10}, alcoxy en C_{1-4}, alkylthio en C_{1-4}, alkylsulfinyle en C_{1-4}, alkylsulfonyle en C_{1-4}, amino, mono(alkyle en C_{1-4})amino, di(alkyle en C_{1-4})amino, (cycloalkyle en C_{3-6})amino, parmi les groupes alkyle en C_{1-15} si R^1 ou R^2 représente un groupe aralkyle en C_{7-12} (ces groupes substituants portant eux-mêmes éventuellement de 1 à 5 substituants identiques ou différents et choisis parmi les atomes d'halogène et les groupes hydroxy, alcoxy en C_{1-4} et alkylthio en C_{1-4}), et parmi les groupes nitro, hydroxy, mercapto, oxo, thioxo, cyano, carbamyle, carboxy, (alcoxy en C_{1-4})carbonyle, sulfo, acylamino en C_{2-6}, acyle en C_{2-4} et (aryle en C_{6-10})carbonyle et les atomes d'halogène,
ou bien R^1 et R^2 représentent, conjointement avec l'atome d'azote voisin, un groupe aziridino, azétidino, pyrrolidino, morpholino ou thiomorpholino.

3. Procédé de préparation d'un composé de formule suivante, ou de l'un de ses sels,



qui comporte le fait de faire réagir un composé de formule



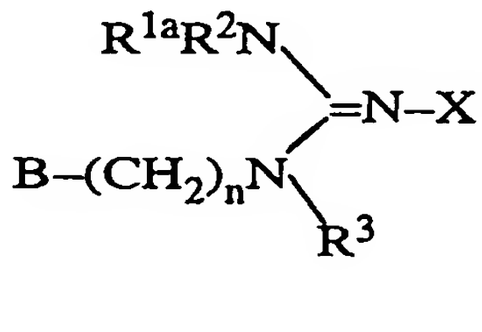
avec un composé de formule

$R^3\text{-}NH(CH_2)_nB$

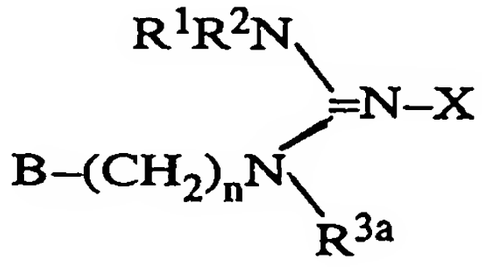
où A, R, X, Y^1 et Y^2 ont les mêmes significations que celles indiquées dans la revendication 1,

n vant 0 ou 1,
B représente un groupe cycloalkyle en C_{3-8}, cycloalcényle en C_{3-8}, aryle en C_{6-14}, thiényle, furyle, pyrrolyle, pyridyle, oxazolyle, thiazolyle, pyrazolyle, imidazolyle, isoxazolyle, isothiazolyle, oxadiazolyle, thiadiazolyle, triazolyle, tétrazolyle, N-oxy-pyridyle, pyrimidinyle, N-oxy-pyrimidinyle, pyridazinyle, pyrazinyle, N-oxy-pyrazinyle, N-oxy-pyridazinyle, benzofuryle, benzothiényle, benzothiazolyle, benzoxazolyle, triazinyle, oxo-triazinyle, tétrazolo[1,5-b]pyridazinyle, triazolo[4,5-b]pyridazinyle, oxo-imidazolyle, dioxo-triazinyle, pyrrolidinyle, pipéridyle, pyranyle, thiopyranyle, oxazinyle, morpholinyle, thiazinyle, pipérazinyle, benzoimidazolyle, quinolyle, isoquinolyle, cinnolinyle, phtalazinyle, quinazolinyle, quinoxalinyle, indolizinyle, quinolizinyle, 1,8-naphtyridinyle, purinyle, ptéridinyle, dibenzofuranyle, carbazolyle, acridinyle, phénanthridinyle, phénazinyle, phénothiazinyle ou phénoxazinyle, qui peut éventuellement porter de 1 à 5 substituants choisis parmi les atomes d'halogène et les groupes alkyle en C_{1-15}, aryle en C_{6-10}, aralkyle en C_{7-10}, cycloalkyle en C_{3-10}, alcényle en C_{2-10}, alcynyle en C_{2-10}, cycloalcényle en C_{3-10}, nitro, hydroxy, mercapto, oxo, thioxo, cyano, carbamyle, carboxy, (alcoxy en C_{1-4})carbonyle, sulfo, alcoxy en C_{1-4}, aryloxy en C_{6-10}, alkylthio en C_{1-4}, arylthio en C_{6-10}, alkylsulfinyle en C_{1-4}, arylsulfinyle en C_{6-10}, alkylsulfonyle en C_{1-4}, arylsulfonyle en C_{6-10}, amino, acylamino en C_{2-6}, mono(alkyle en C_{1-4})amino, di(alkyle en C_{1-4})amino, (cycloalkyle en C_{3-6})amino, arylamino en C_{6-10}, acyle en C_{2-4}, (aryle en C_{6-10})carbonyle, thiényle, furyle, pyrazolyle, thiazolyle, isothiazolyle, oxazolyle, isoxazolyle, imidazolyle, triazolyle, tétrazolyle, pyridyle, pyrimidinyle, pyridazinyle, quinolyle, isoquinolyle et indolyle, et
R^3 représente un atome d'hydrogène ou un groupe alkyle en C_{1-10} linéaire, ramifié ou cyclique, alcényle en C_{2-10}, alcynyle en C_{2-10} ou aralkyle en C_{7-12}, lequel groupe peut éventuellement porter de 1 à 5 substituants identiques ou différents et choisis parmi les groupes cycloalkyle en C_{3-10}, cycloalcényle en C_{3-10}, aryloxy en C_{6-10}, arylthio en C_{6-10}, arylsulfinyle en C_{6-10}, arylsulfonyle en C_{6-10}, arylamino en C_{6-10}, thiényle, furyle, pyrazolyle, thiazolyle, isothiazolyle, oxazolyle, isoxazolyle, imidazolyle, triazolyle, tétrazolyle, pyridyle, pyrimidinyle, pyridazinyle, quinolyle, isoquinolyle, indolyle, parmi les groupes aryle en C_{6-10} et aralkyle en C_{7-10} si R^3 représente un groupe aralkyle en C_{7-12} (ces groupes substituants portant eux-mêmes éventuellement de 1 à 5 substituants identiques ou différents et choisis parmi les atomes d'halogène et les groupes hydroxy, alkyle en C_{1-4}, alcényle en C_{2-4}, alcynyle en C_{2-4}, aryle en C_{6-10}, alcoxy en C_{1-4}, phénoxy, alkylthio en C_{1-4} et phénylthio), parmi les groupes alcényle en C_{2-10}, alcynyle en C_{2-10}, alcoxy en C_{1-4}, alkylthio en C_{1-4}, alkylsulfinyle en C_{1-4}, alkylsulfonyle en C_{1-4}, amino, mono(alkyle en C_{1-4})amino, di(alkyle en C_{1-4})amino, (cycloalkyle en C_{3-6})amino, parmi les groupes alkyle en C_{1-15} si R^3 représente un groupe aralkyle en C_{7-12}, (ces groupes substituants portant eux-mêmes éventuellement de 1 à 5 substituants identiques ou différents et choisis parmi les atomes d'halogène et les groupes hydroxy, alcoxy en C_{1-4} et alkylthio en C_{1-4}), et parmi les groupes nitro, hydroxy, mercapto, oxo, thioxo, cyano, carbamyle, carboxy, (alcoxy en C_{1-4})carbonyle, sulfo, acylamino en C_{2-6}, acyle en C_{2-4} et (aryle en C_{6-10})carbonyle et les atomes d'halogène.

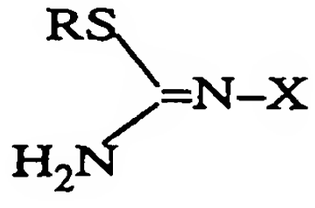
4. Procédé de préparation d'un composé de formule suivante, ou de l'un de ses sels,



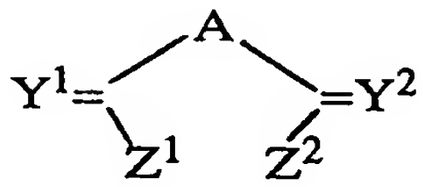
ou



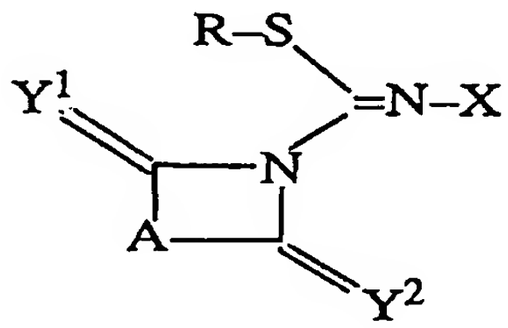
qui comporte le fait de faire réagir un composé de formule



avec un composé de formule



et le fait de faire ensuite réagir le composé ainsi obtenu, de formule



1) avec une amine de formule

$$R^1R^2NH$$

ou avec un sel d'une telle amine, puis avec un composé de formule

$$R^3\text{-}NH(CH_2)_n\text{-}B$$

après acylation, si nécessaire, quand R^1 représente un atome d'hydrogène, ou bien
2) avec un composé de formule

$$R^3\text{-}NH(CH_2)_n\text{-}B$$

puis avec une amine de formule

$$R^1R^2NH$$

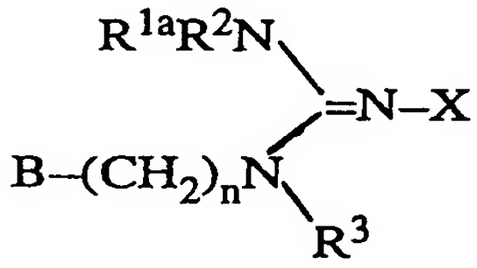
ou avec un sel d'une telle amine,

après acylation, si nécessaire, quand R^3 représente un atome d'hydrogène,

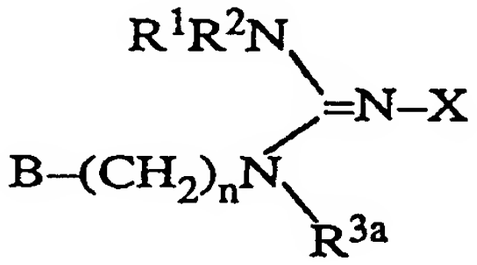
où A, R, X, Y^1, Y^2, Z^1 et Z^2 ont les mêmes significations que celles indiquées dans la revendication 1,
B, n, R^1, R^2 et R^3 ont les mêmes significations que celles indiquées dans les revendications 2 et 3,
R^{1a} a la même signification que R^1, mais peut en outre représenter un groupe acyle en $C_{1\text{-}10}$ aliphatique, alicyclique, aromatique ou hétérocyclique, lequel groupe peut éventuellement porter de 1 à 5 substituants identiques ou différents et choisis parmi les groupes cycloalkyle en $C_{3\text{-}10}$, cycloalcényle en $C_{3\text{-}10}$, aryloxy en $C_{6\text{-}10}$, arylthio en $C_{6\text{-}10}$, arylsulfinyle en $C_{6\text{-}10}$, arylsulfonyle en $C_{6\text{-}10}$, arylamino en $C_{6\text{-}10}$, aryle en $C_{6\text{-}10}$, aralkyle en $C_{7\text{-}10}$, thiényle, furyle, pyrazolyle, thiazolyle, isothiazolyle, oxazolyle, isoxazolyle, imidazolyle, triazolyle, tétrazolyle, pyridyle, pyrimidinyle, pyridazinyle, quinolyle, isoquinolyle, indolyle, (ces groupes substituants portant eux-mêmes éventuellement de 1 à 5 substituants identiques ou différents et choisis parmi les atomes d'halogène et les groupes hydroxy, alkyle en $C_{1\text{-}4}$, alcényle en $C_{2\text{-}4}$, alcynyle en $C_{2\text{-}4}$, aryle en $C_{6\text{-}10}$, alcoxy en $C_{1\text{-}4}$, phénoxy, alkylthio en $C_{1\text{-}4}$ et phénylthio), alcényle en $C_{2\text{-}10}$, alcynyle en $C_{2\text{-}10}$, alcoxy en $C_{1\text{-}4}$, alkylthio en $C_{1\text{-}4}$, alkylsulfinyle en $C_{1\text{-}4}$, alkylsulfonyle en $C_{1\text{-}4}$, amino, mono(alkyle en $C_{1\text{-}4}$)amino; di(alkyle en $C_{1\text{-}4}$)amino, (cycloalkyle en $C_{3\text{-}6}$)amino, alkyle en $C_{1\text{-}15}$ (ces groupes substituants portant eux-mêmes éventuellement de 1 à 5 substituants identiques ou différents et choisis parmi les atomes d'halogène et les groupes hydroxy, alcoxy en $C_{1\text{-}4}$ et alkylthio en $C_{1\text{-}4}$), nitro, hydroxy, mercapto, oxo, thioxo, cyano, carbamyle, carboxy, (alcoxy en $C_{1\text{-}4}$)carbonyle, sulfo, acylamino en $C_{2\text{-}6}$, acyle en $C_{2\text{-}4}$ et (aryle en $C_{6\text{-}10}$)carbonyle et les atomes d'halogène,
ou bien R^{1a} et R^2 représentent, conjointement avec l'atome d'azote voisin, un groupe amino cyclique, et
R^{3a} a la même signification que R^3, mais peut en outre représenter un groupe acyle en $C_{1\text{-}10}$ aliphatique, alicyclique, aromatique ou hétérocyclique, lequel groupe peut éventuellement porter de 1 à 5 substituants identiques ou

différents et choisis parmi les groupes cycloalkyle en C_{3-10}, cycloalcényle en C_{3-10}, aryloxy en C_{6-10}, arylthio en C_{6-10}, arylsulfinyle en C_{6-10}, arylsulfonyle en C_{6-10}, arylamino en C_{6-10}, aryle en C_{6-10}, aralkyle en C_{7-10}, thiényle, furyle, pyrazolyle, thiazolyle, isothiazolyle, oxazolyle, isoxazolyle, imidazolyle, triazolyle, tétrazolyle, pyridyle, pyrimidinyle, pyridazinyle, quinolyle, isoquinolyle, indolyle, (ces groupes substituants portant eux-mêmes éventuellement de 1 à 5 substituants identiques ou différents et choisis parmi les atomes d'halogène et les groupes hydroxy, alkyle en C_{1-4}, alcényle en C_{2-4}, alcynyle en C_{2-4}, aryle en C_{6-10}, alcoxy en C_{1-4},phénoxy, alkylthio en C_{1-4} et phénylthio), alcényle en C_{2-10}, alcynyle en C_{2-10}, alcoxy en C_{1-4}, alkylthio en C_{1-4}, alkylsulfinyle en C_{1-4}, alkylsulfonyle en C_{1-4}, amino, mono(alkyle en C_{1-4})amino, di(alkyle en C_{1-4})amino, (cycloalkyle en C_{3-6})amino, alkyle en C_{1-15} (ces groupes substituants portant euxmêmes éventuellement de 1 à 5 substituants identiques ou différents et choisis parmi les atomes d'halogène et les groupes hydroxy, alcoxy en C_{1-4} et alkylthio en C_{1-4}), nitro, hydroxy, mercapto, oxo, thioxo, cyano, carbamyle, carboxy, (alcoxy en C_{1-4})carbonyle, sulfo, acylamino en C_{2-6}, acyle en C_{2-4} et (aryle en C_{6-10})carbonyle et les atomes d'halogène.

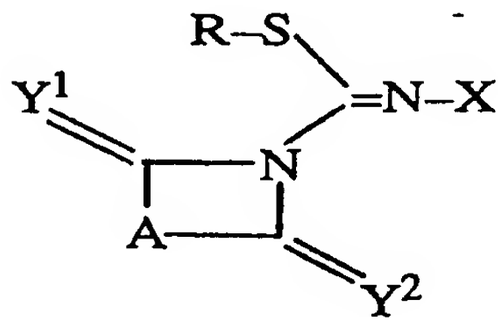
5. Procédé de préparation d'un composé de formule suivante, ou de l'un de ses sels,



ou



qui comporte le fait de faire réagir un composé de formule



1) avec une amine de formule

$$R^1R^2NH$$

ou avec un sel d'une telle amine, puis avec un composé de formule

$$R^3\text{-}NH(CH_2)_n\text{-}B$$

après acylation, si nécessaire, quand R^1 représente un atome d'hydrogène, ou bien
2) avec un composé de formule

$$R^3\text{-}NH(CH_2)_n\text{-}B$$

puis avec une amine de formule

R^1R^2NH

ou avec un sel d'une telle amine,

après acylation, si nécessaire, quand R^3 représente un atome d'hydrogène,
où A, R, X, Y^1 et Y^2 ont les mêmes significations que celles indiquées dans la revendication 1,
B, n, R^1, R^2 et R^3 ont les mêmes significations que celles indiquées dans les revendications 2 et 3, et
R^{1a} et R^{3a} ont les mêmes significations que celles indiquées dans la revendication 4.

6. Procédé conforme à l'une des revendications 1 à 5, dans lequel R représente un groupe alkyle en C_{1-10} ou aralkyle en C_{7-12}.

7. Procédé conforme à l'une des revendications 1 à 5, dans lequel A représente un groupe alkylène en C_{1-4} choisi parmi les suivants :

$-CH_2-$, $-CH_2CH_2-$, $-CH_2CH_2CH_2-$, $-(CH_2)_4-$,

$$-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-,\quad -CH_2\,\underset{\displaystyle CH_3}{\underset{|}{CH}}CH_2-\quad\text{et}\quad -\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2\,CH_2-.$$

8. Procédé conforme à l'une des revendications 1 à 5, dans lequel A représente un groupe o-phénylène, 1,2-éthylène ou 1,3-propylène.

9. Procédé conforme à l'une des revendications 1 à 5, dans lequel le groupe électroattracteur X est un groupe cyano ou nitro.

10. Procédé conforme à la revendication 2 ou 5, dans lequel ledit groupe R^1R^2N est un groupe amino sans substituants, mono(alkyle en C_{1-4})amino ou di(alkyle en C_{1-4})amino.

11. Procédé conforme à la revendication 4 ou 5, dans lequel R^{1a} représente un groupe alkyle en C_{1-10}, aralkyle en C_{7-12} ou acyle en C_{1-4}.

12. Procédé conforme à la revendication 4 ou 5, dans lequel ledit groupe $R^{1a}R^2N$ est un groupe amino sans substituants, mono(alkyle en C_{1-4}(amino, di(alkyle en C_{1-4})amino, (acyle en- C_{1-4})amino ou N-(acyle en C_{1-2})-N-(alkyle en C_{1-4})amino.

13. Procédé conforme à l'une des revendications 3 à 5, dans lequel B représente un groupe pyridyle ou thiazolyle qui peut porter un ou deux atomes d'halogène en tant que substituants.

14. Procédé conforme à la revendication 4 ou 5, dans lequel R^{3a} représente un groupe alkyle en C_{1-10} ou aralkyle en C_{7-12}.

15. Procédé conforme à la revendication 2, 4 ou 5, dans lequel ledit groupe R^1R^2N est un groupe amino sans substituants, mono(alkyle en C_{1-4})amino, di(alkyle en C_{1-4})amino, aziridino, azétidino, pyrrolidino, morpholino ou thiomorpholino.